Lecture Experiments in Analytical Chemistry

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ИЗДАТЕЛЬСТВО
МИР

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Аа	a	Зз	z	Пп	p	Цц	ts
Бб	b	Ии	i	Рр	r	Чч	ch
Вв	v	Кк	k	Сс	s	Шш	sh
Гг	g	Лл	l	Тт	t	Щщ	shch
Дд	d	Мм	m	Уу	u	ЭЭ	e
Ее	e	Нн	n	Фф	f	Юю	yu
Жж	zh	Оо	o	Хх	kh	Яя	ya

На английском языке

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PREFACE

The demonstrative experiment is part and parcel of a modern lecture on chemistry. The success of a lecture depends to a certain extent on the correct selection and timely conduction of an experiment or on a demonstration of slides and tables. This textbook is the first attempt of its kind in generalizing the experience gained in the demonstrative experiment at lectures on analytical chemistry. It is based on the experience of the department of analytical chemistry of the Lomonosov Moscow State University. Moreover, demonstrations found in the textbooks of general chemistry that conform to the specificity of analytical chemistry are used.

Attention is mainly devoted to the correctness and experidency of selecting an experiment and to its place in the general layout of a lecture, since the purpose of an experiment is to make the material being studied more convincing. The authors have classified the experiments according to the principal sections of the theory of analytical chemistry adopted in the programme for universities. Recommendations concerning the make-up of introductory lectures on qualitative and quantitative analysis have been separated into special chapters. The description of experiments is preceded by a brief general part dealing with the essence of an experiment and the chemism of the phenomena being observed. Due to the diversity of the questions dealt with in the book, the material is expounded somewhat schematically in some cases.

The textbook has ample table material, which may be used for preparing slides. The values of stability constants of complex compounds and the values of solubility products have been taken from the handbook by L. G. Sillen

and A. E. Martell, *Stability Constants of Metal-Ion Complexes*, the Chemical Society, V. 1. London, Burlington House, 1964. Supplement No. 1, 1971.

Attention is particularly devoted to the equipment of the auditorium where lectures on chemistry are read, and advice is given on the make-up of a lecture. Due to technical difficulties, it is possibly not everywhere that some recommendation may be fulfilled. The textbook gives a considerably greater number of experiments than the lecture time allows, and the lecturer has a choice.

The authors express their gratitude to the workers of the department of analytical chemistry of the Moscow State University Prof. V. M. Peshkova, D. Sc. (Chem.), and Prof. P. K. Agasyan, D. Sc. (Chem.), for the valuable advice which they gave on reading the manuscript. We would also be grateful to all readers for their remarks, suggestions and addenda concerning the conduction of a chemical experiment at lectures on analytical chemistry.

Authors

CHAPTER I

General information

Many books and articles have been written on the importance of an experiment at lectures on chemistry [1-6]. It should merely be emphasized that the technique of conducting an experiment is of especial importance at lectures on analytical chemistry, since together with the demonstration of a phenomenon, an experiment is also a demonstration of the correct methods of work of an analyst. The introduction of new or the perfection of old equipment makes it possible for the lecturer to give the listeners material which could not be presented before due to the difficulty or impossibility of demonstration. Changes in the existing equipment, such as automatic projection in an illuminated auditorium, the utilization of television, and a fitted-out place for the listener and the lecturer will contribute to the success of a lecture.

EQUIPMENT OF THE AUDITORIUM

Demonstration table. Experiments may be demonstrated on either a lecturer's table or on a specially fitted-out table. Water, gas and electric current (alternating current with a voltage of 127 V and 220 V, and direct current with a voltage of 20 V) must be laid on to the table. It is desirable that a sink should be built into the demonstration table. A panel with clamps and knife switches for switching on the light and the epidiascope, lowering the blinds, and so forth, should be on or near the table. This makes it possible for the assistant to quickly carry out the necessary operation at any moment. For experiments on

analytical chemistry, local exhaust ventilation is not essential.

The demonstration table should be sufficiently broad, its recommended size being 1.2 m × 2 m. The table should have special lighting for illuminating the demonstration

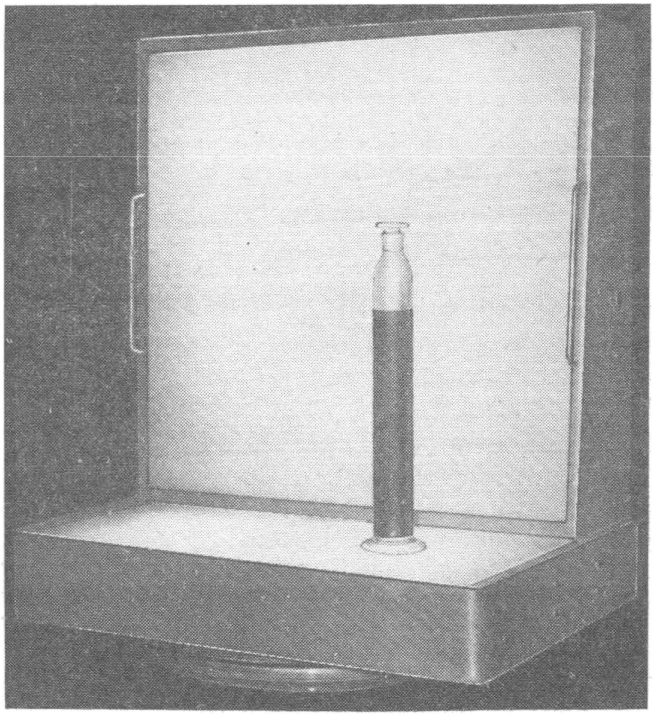


Fig. I-1. Screen with illumination for demonstrating coloured solutions

material of a lecture. This lighting may be a soffit over the table or lamps on the table that are cased from the side of the audience. Screens and specially-built boxes may be used for observing coloured solutions (Fig. I-1). The lecturer's reading desk with lighting (Fig. I-2) and a microphone or a tape recorder should be on the table. A portable microphone which does not restrict the lecturer in his motions, being attached to his suit, is very convenient.

Blackboard. The blackboard on which the lecturer writes must be large. The most convenient blackboard is with moving cloth in the form of an endless belt on two rollers with manual rotation or an automatic device for starting and stopping the belt. Devices with two balanced blackboards are also widely used: a blackboard with a written text rises and the text is written on the lower blackboard, and then they are reversed.

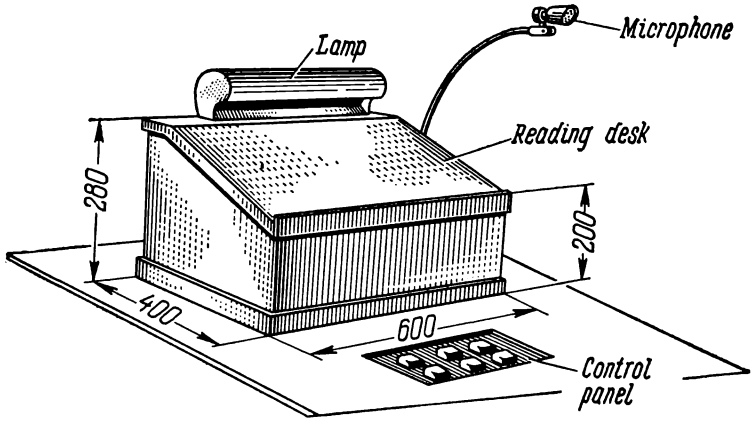


Fig. I-2. Lecturer's reading desk

The length of the moving cloth for a 45-minute lecture should be at least 25 m, and its breadth, 2 m. It is desirable that the colour of linoleum or plastic should be dark green (this colour is the least tiresome for the eyes) or black. Brown colour is undesirable: the contrast is poor against this background, and the eyes quickly get tired. Pieces of chalk should be slightly sharpened, and one of the ends should be wrapped in paper. The following method of preparing chalk that does not soil the fingers may be proposed: put pieces of chalk into a saturated solution of acrylic acid in dichloroethane for two hours, and then dry them.

In plotting diagrams or graphs on the blackboard, it is convenient for the lecturer to use colour chalk or colour crayons. The board should be erased with a damp well-wrung sponge or a piece of foamed plastic.

Projectors and screens. The epidiascope is used to demonstrate illustrations, photographs of 8 cm × 8 cm-9 cm × 12 cm, and some sufficiently flat objects. Moreover, it is desirable that the auditorium should have a projector for demonstrating slides of 5 cm × 5 cm made of film in plastic frames. Such projectors may have a magazine cassette and remote control for changing the slides and focusing. The slides should be shown in a semi-dark auditorium so that the listeners could sketch an illustration or write down a table. After the lecturer finishes his explanations, an image should be held for several seconds.

Small auditorium are darkened with ordinary curtains, while large auditoriums should have automatically moving curtains.

The quality of slide projection depends on illumination. In projecting black-and-white slides, it is sufficient to have an illumination of 50 lux, but not less than 25 lux. The brightness of an image depends on the properties of the reflecting surface of the screen. The coefficients of reflection of mat surfaces of some materials are given below:

Drawing paper	0.45-0.55
White linen	0.55-0.60
Aluminium	0.55-0.65
Zinc white	0.72
Barium sulphate	0.96

Barium sulphate has the highest coefficient of reflection; therefore, it is used most often for covering the reflecting surface of diffuser screens [7]. Use is also made of directed diffuser screens, which reflect the light flux in a certain direction, thus increasing the brightness of the reflecting surface; for example, the so-called pearl screen (covered with a layer of small glass balls), the raster-type screen (consisting of many small lenses) and metallized screens. The surface of the directed diffuser screens may be 3-4 times brighter, and the surface of raster-type screens, 15 times brighter than that of the diffuser screen.

In reading lectures on some themes, it is useful to show short educational films [8]. The modern auditorium should have the appropriate equipment for this purpose. Television may be used to demonstrate experiments which can-

not be performed directly in the auditorium, and also to show laboratory or some other equipment, and so forth [9].

Protective screens. Protective screens must be used when experiments with solutions that may spray are demonstrated. The screens may be made of glass or plexiglas (Fig. I-3). It is desirable to have several screens of different dimensions.

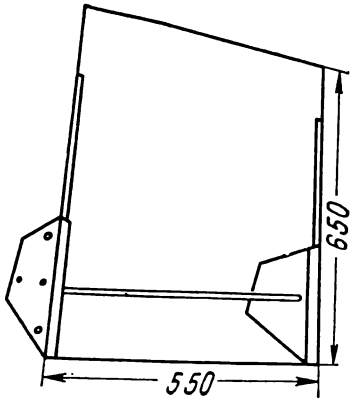


Fig. I-3. Protective screen made of plexiglas

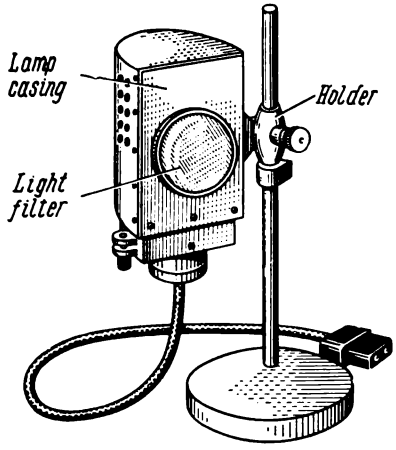


Fig. I-4. ОИ-18 luminescent illuminator

For examining coloured solutions, a white screen should be put behind a cylinder, and in experiments with the formation of white precipitates, a black screen should be put.

Pointer. The pointer should be conical. It may be of wood, glass-plastic or bamboo. The recommended length of the pointer is 1.5-2 m. It is desirable that the pointer should be white (for showing something on the blackboard), but the tip, approximately 3-6 cm long, should be dark (for demonstrating tables). It is convenient to use a light-beam pointer, which is a flashlight with a narrow directed beam of light (in the form of an arrow) that enables the lecturer to demonstrate table material without leaving the desk.

Clock. A large clock (desirably with a luminous dial) should be on a wall in the auditorium, enabling the lecturer to correlate lecture material with time.

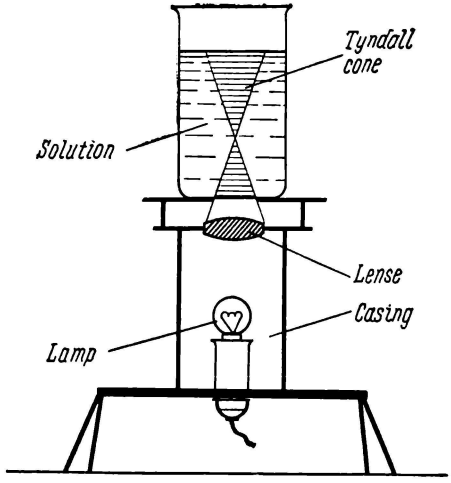


Fig. I-5. Illuminator for observing the Tyndall effect

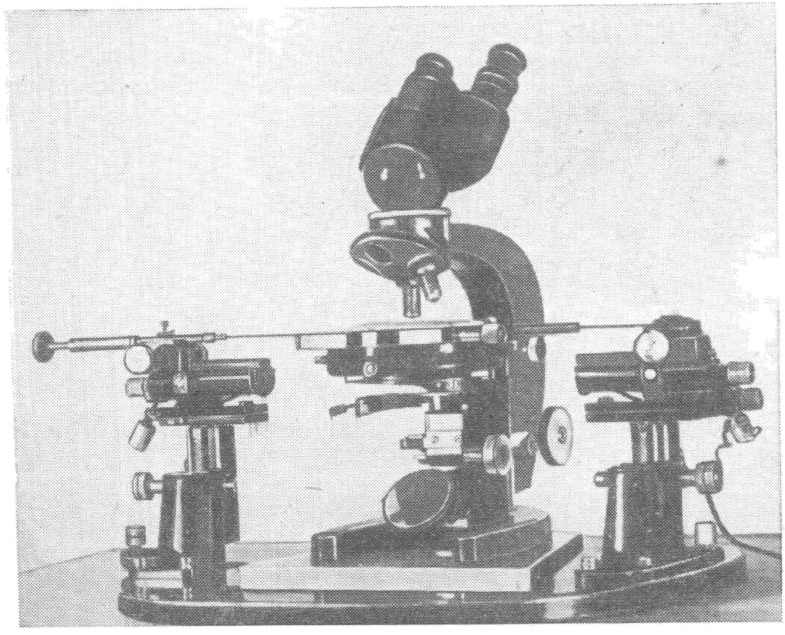


Fig. I-6. Microscope with manipulators

Special instruments. Apart from the ordinary auditorium equipment, special instruments are needed for performing some experiments. For experiments in analytical chemistry, there should be the following instruments: a computing and recording unit with an audio amplifier for experiments with radioactive isotopes, a luminescent illuminator (Fig. I-4), a metronome, an illuminator for experiments with colloidal solutions (Fig. I-5), a pH-meter, a microscope, a microscope with manipulators for ultramicroanalysis (Fig. I-6), automatic titrators, a direct-vision spectroscope, and chromatographic columns (Fig. I-7).

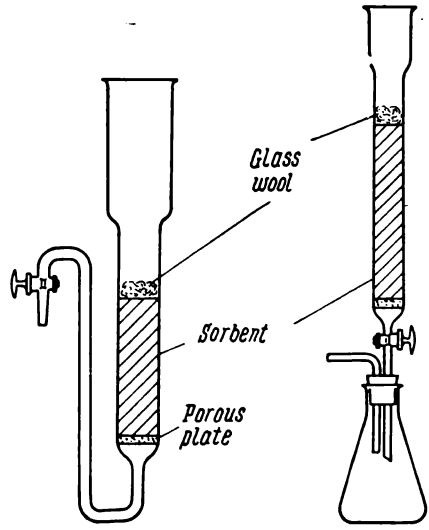


Fig. I-7. Chromatographic columns

DEMONSTRATION MATERIAL

Tables and graphs. Tables are important at a lecture. They save the lecturer's time and help the listeners to understand the lecture better. Tables should be plotted on sufficiently large sheets of white paper. For a large auditorium, the recommended size is 2 m $\times$ 1.5 m. All the letters and figures should be large, and the lines sufficiently thick, so that they would be seen well from the back rows of the auditorium. For greater clarity, separate parts of graphs or structural formulas are written in India ink; either red or yellow, but not dark blue, since the dark blue colour is poorly distinguishable from black at a distance. It is recommended to cover the tables with varnish which painters use; then, the tables do not spoil and are easily cleaned with a damp piece of cloth. If possible, tables drawn on white Whatman paper should be pasted to cloth.

Tables are fastened to wooden rods at the top and desirably at the bottom. A cord is attached to the rod. Tables may be hung on special supports with moving planks and hooks. In some cases, it is more convenient to stretch a steel wire with movable hooks along the wall. If possible, blocks with rods moving up and down are made on special cantilevers fixed to the ceiling in the auditorium. Tables that are not too heavy should be fastened with magnetic bars to iron plates, which are fixed in the wall and painted in the same colour as the walls.

A chemical auditorium must have the Mendeleev periodic table of elements. A luminous table is convenient and effective. By using a special panel on the demonstration table, a lecturer may switch on the lighting of separate cells with symbols of elements or whole groups and periods. It is desirable to have also a movable table with expanded periods, which is demonstrated when necessary.

Recommendations concerning the content and design of tables will be given in the appropriate sections of this book.

Slides. Large slides, 8 cm × 8 cm and 9 cm × 12 cm, are prepared on a positive plate or a thick photographic film. To protect the emulsion layer, the photographic plate is covered with thin glass and framed with black paper. In some cases, illustrations are drawn on the gelatin layer of the slides. For this purpose, silver bromide is first removed from photographic emulsion by treatment with sodium thiosulphate, and then the slides are washed and dried. Slides made on a standard black-and-white photographic plate may be directly projected on the screen. However, a white image seems poor against a dark background; from a negative, therefore, it is better to make a positive print on a low-sensitive positive film. It is recommended to use slides made of reversible colour film taken from a colour diagram or a colour catalogue, and so forth. The film is then cut, and separate exposures are put in plastic or cardboard frames.

Slides should be taken from drawings and illustrations having a size of 18 cm × 24 cm and drawn in black India ink on white paper. The thickness of auxiliary lines, letters and figures should be 0.2-0.4 mm, and the thickness

of curves, 0.7-1 mm. A numbered paper circle should be pasted to the lower left-hand corner of the slide frame (Fig. I-8). The mark helps the assistant to immediately put the plate correctly into the projector in the darkness.

A lecture should not be overloaded with a great number of tables and slides. In expounding theoretical questions, it is best to demonstrate 4-5 tables and 3-4 slides. Their number may be increased at introductory and concluding

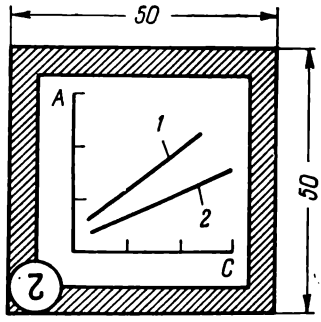


Fig. I-8. Example of a slide

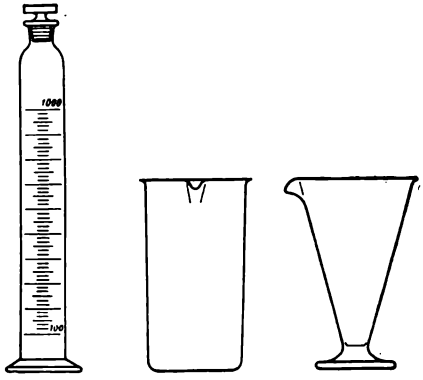


Fig. I-9. Ware for conducting experiments

lectures. Illustrations and tables should not be supersaturated with information, since an excessively saturated illustration or a table is poorly perceived when viewed for a short time (30-40 sec).

Ware. In conducting reactions in solutions, use should be made of graduated cylinders with ground-glass stoppers and a capacity of at least 0.5-1 litre. A cylinder should be sufficiently stable (Fig. I-9). Tall Bunsen beakers (capacity: 1 litre) and measuring glasses (Fig. I-9) may also be used, but it is less convenient to mix solutions in them.

All reagents are kept in bottles or jars with ground-glass stoppers and a capacity of 300 ml (Fig. I-10). Reagents which decompose when exposed to light are put in bottles made of dark glass. Solutions of alkalies and fluorides should be kept in polyethylene vessels. All bottles with reagents should have sufficiently large labels with

inscriptions (a formula or the name of a reagent, its concentration). For example, CH_3COONa, saturated solution; dithizone, 0.1 per cent solution in CCl_4, and so forth. When necessary, cylinders with solutions or precipitates should likewise have labels, which are fastened by a special holder (Fig. I-11). Moreover, it is necessary to have funnels, pipettes, burettes, droppers, test tubes, flasks, beakers and other devices of different dimensions, and also a special cuvette for carrying out experiments with radioactive substances, mercury or concentrated acids.

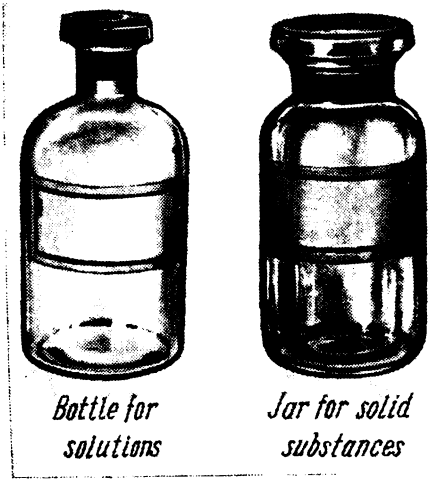


Fig. I-10. Ware for keeping reagents

Other demonstration material. Demonstration material placed on the demonstration table during a lecture is of great assistance to the lecturer. Students may familiarize themselves with it independently during a break or after a lecture. Such material is a set of specimens of ores, minerals, alloys, and so forth. Such sets should be beautifully designed. Special boxes with cells may be made for separate specimens, or supports may be made from plexiglas or metal. Every specimen has an inscription bearing its name, formula or chemical composition. It is desirable to indicate the place from which the specimen has been taken. A set should have a homogeneous mineral (such as halite), a heterogeneous mineral (granite), a schistose mineral (mica), and coloured and colourless minerals [10]. Moreover, a set should have alloys of iron, of copper, and of aluminium and other alloys, and also alloys of rare elements with an indication of their composition.

It is desirable to make models of different crystal lattices, such as AgCl, $BaSO_4$ and $K_2[PtCl_6]$, which are made

of multi-coloured wooden or metallic balls fastened with rods (Fig. I-12). A lattice may also be made of plexiglas with fixed-in balls. Every model has a tag with an inscription (the type of the lattice, the formula of the compound, and the symbols of atoms of the lattice). For example, $K_2[PtCl_6]$, tetragonal system, K = red, Pt = white, Cl = = green.

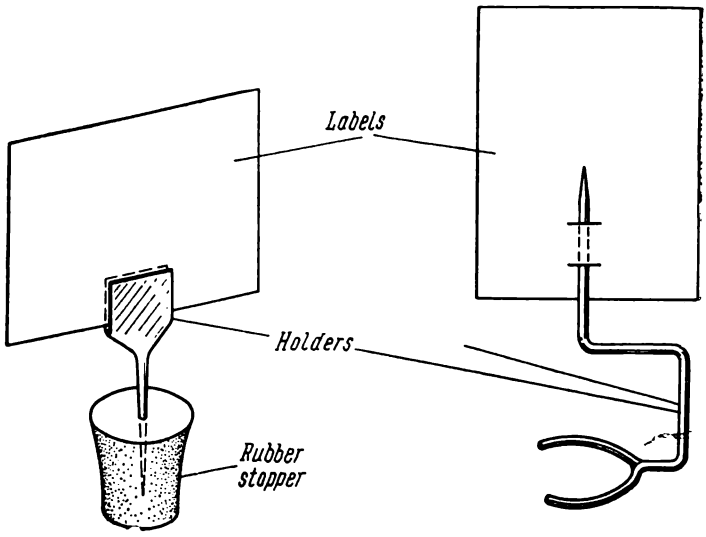
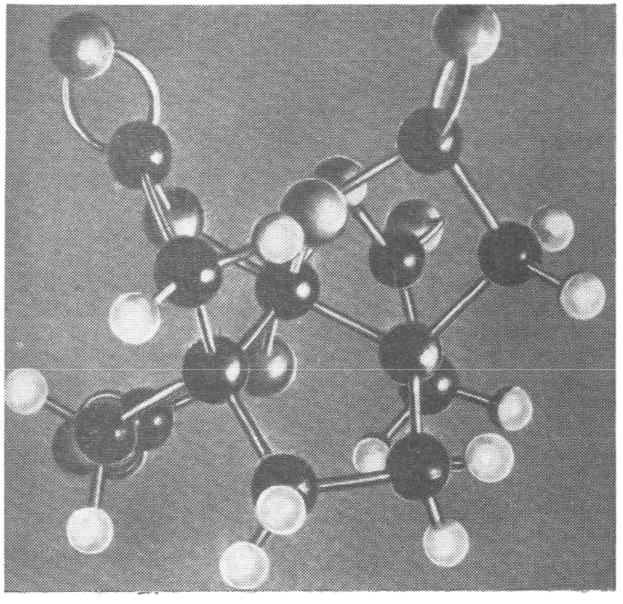


Fig. I-11. Label holders

It is useful to present to the listeners books and magazines on a question being discussed. They should be laid out on the demonstration table or on a table near the lecturer.

Storage of demonstration material. A chemical auditorium as a rule has a lecture cabinet for keeping lecture instruments, reagents, ware, and so forth. Tables should be kept in a special closet, away from heaters. They should be numbered, selected according to lecture themes, and hung according to numbers. A list of tables should be drawn up according to numbers. Instruments are kept in a special closet. Separate shelves are used for keeping ware; special boxes with cells may be used. Bottles and jars with reagents should be kept in a separate closet.



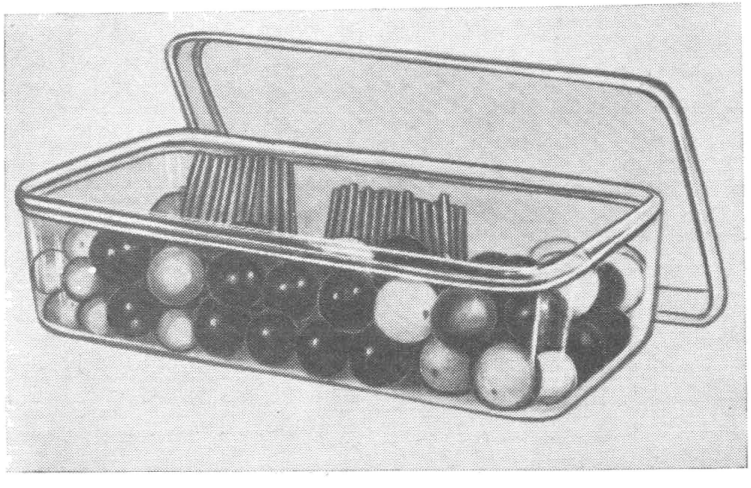


Fig. I-12. Model of a crystal lattice of calcium EDTA complexes and a set of balls

PREPARATION AND CONDUCTION OF AN EXPERIMENT

As a rule, the lecturer discusses experiments to be conducted at a coming lecture with his assistant one or two days in advance. All experiments should be verified. This is very important, since it has often been observed that even the simplest experiment may not turn out if it is not carefully prepared and verified. All ware should be washed and rinsed with distilled water, and all reagents should be prepared anew. The experiment is then conducted in the way it would be conducted at the lecture (it is important to note the duration of the experiment). If an experiment is carried out for the first time, it may be conducted first with a small amount of reagents. Then, it is necessary to check the work of the required instruments, and also look over the entire demonstration material, replace obsolete or add new parts, and select the necessary tables.

Prior to a lecture, it is necessary to cover the demonstration table with white paper and arrange the ware and demonstration material according to a plan drawn up beforehand. It is necessary to check the motion of the blackboard and to see whether the lights, the epidiascope, the motion-picture projector, the microphone and the blackout work. Then, it is necessary to put the pointer, chalk, sponge or a piece of cloth, and to hang the necessary tables and prepare the screen.

The following order of arranging the material on the demonstration table may be recommended. Cylinders with solutions or precipitates in which an experiment is to be conducted should be arranged in the order of the performance of experiments from the left to the right (from the side of the audience). The experiments are conducted in the same order. If it is necessary to separate a solution into several parts, the solution should be in the left cylinder. Bottles with solutions are placed in front of cylinders from the assistant's side, and labels should be turned towards the audience. Colour chalks and a pointer should be put next to the lecturer's reading desk. Books and journals are put farther away from the place where an experi-

ment is to be conducted (it is better to put them on the other side of the reading desk). Protective, white and black screens should be put next to the demonstration table.

The assistant should look beforehand at everything on the table from the back rows of the auditorium, making sure that everything is illuminated well enough and that all the necessary details are seen.

An experiment is as a rule conducted when material is being expounded. The lecturer makes a sign to the assistant for performing an experiment or showing a slide, darkening the auditorium, and so forth. The assistant should perform an experiment in time. He should not hasten to come to the table, since the lecturer may not have time to expound the entire material and would unintentionally hurry, but there should also be no delay, since every minute of a lecture is valuable. Usually, the lecturer makes explanations during an experiment and comments on the result (the assistant himself can do this). After performing a reaction, the assistant moves a cylinder forward and puts, when necessary, a white or black screen behind it. All bottles and cylinders must be stoppered. In removing a stopper from a cylinder or from a bottle containing a reagent, the assistant should put it on a sheet of filter paper prepared in advance (do not mix up the stoppers, as this may make an impression of carelessness, not to mention the fact that the experiment may be spoiled). If there are some discrepancies during an experiment, they should be logged.

After a lecture is over, the assistant puts all the demonstration material into the lecture closet, setting everything in the proper place, hangs the tables in the established order according to the numbers, washes the entire ware without fail (this is especially important after experiments with fluorides or poorly soluble precipitates), and pours out reagent solutions which cannot be kept (hydrogen-sulphide water, and so forth). Immediately after a lecture, it is necessary to discuss the demonstrations with the lecturer and write down the remarks or suggestions in a special notebook.

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CHAPTER II

Introduction to qualitative analysis

The introductory lecture is especially important. The listeners' interest in the subsequent lectures depends on its success. At the introductory lecture on qualitative analysis, the classification of methods according to the way of performance and according to the amount of the substance being analyzed is usually discussed, and the principal characteristics of analytical reactions are expounded. The students should immediately get an idea about the real objects of an investigation; therefore, it is expedient to put on the table boxes with specimens of ores, minerals, alloys, fertilizers, and so forth. The lecturer tells about the role of chemical analysis and its conduction in the laboratory and in the field. It is recommended to show a field laboratory (Fig. II-1) and the workplace of an analyst (Fig. II-2).

In comparing the analytical methods according to the amount of the substance being analyzed, the following set of ware should be presented.

Macroanalysis. A beaker with a capacity of 300-400 ml, a conical flask with a capacity of 300 ml, a chemical funnel ($d = 7$ cm) with a filter that is fixed to a holder, a porcelain bowl ($d = 10$ cm), a washer with a capacity of 300-500 ml, a watch glass ($d = 10$ cm), a porcelain crucible ($d = 3$ cm), and test tubes in a stand ($l = 20$ cm, $d = 2.5$ cm).

Semimicroanalysis. A beaker with a capacity of 20 ml, a conical flask with a capacity of 20 ml, a chemical funnel ($d = 2.5$ cm), a washer with a capacity of 100 ml, a crucible ($d = 1.5$ cm), a porcelain bowl ($d = 3$ cm), and centrifugal test tubes in a stand ($l = 5$ cm, $d = 1$ cm).

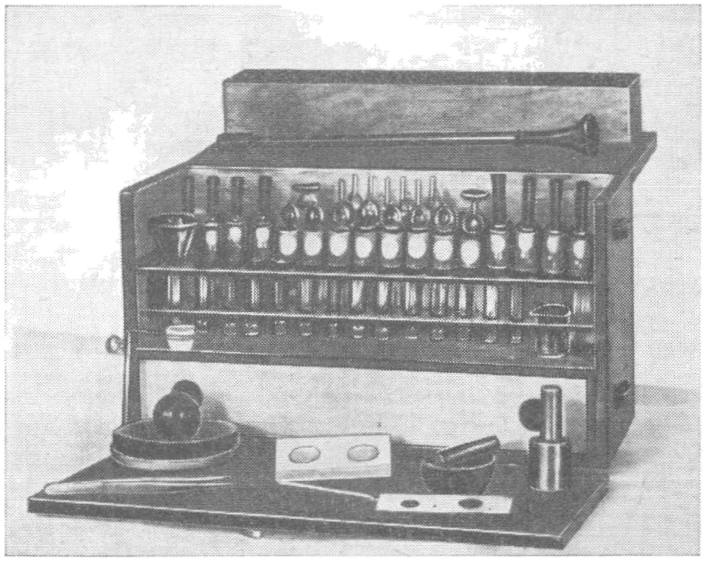


Fig. II-1. Chemical field laboratory

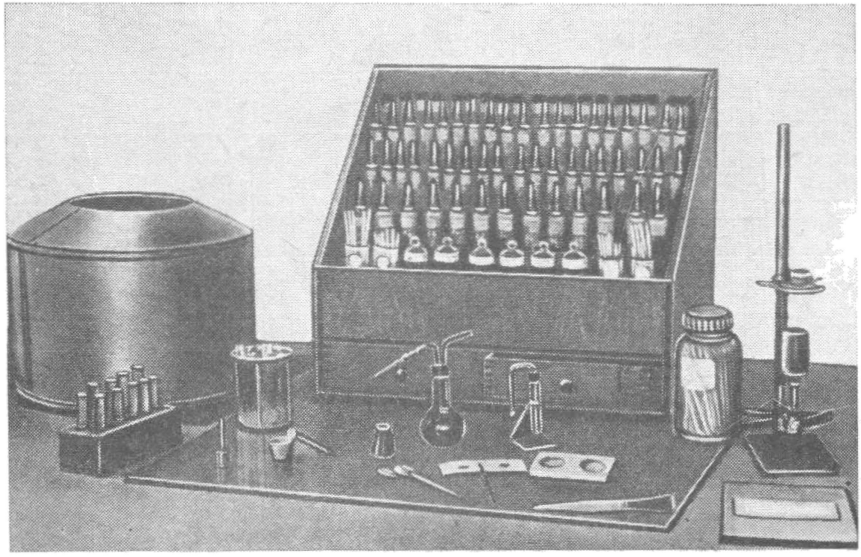


Fig. II-2. Workplace of an analyst in a laboratory of qualitative analysis

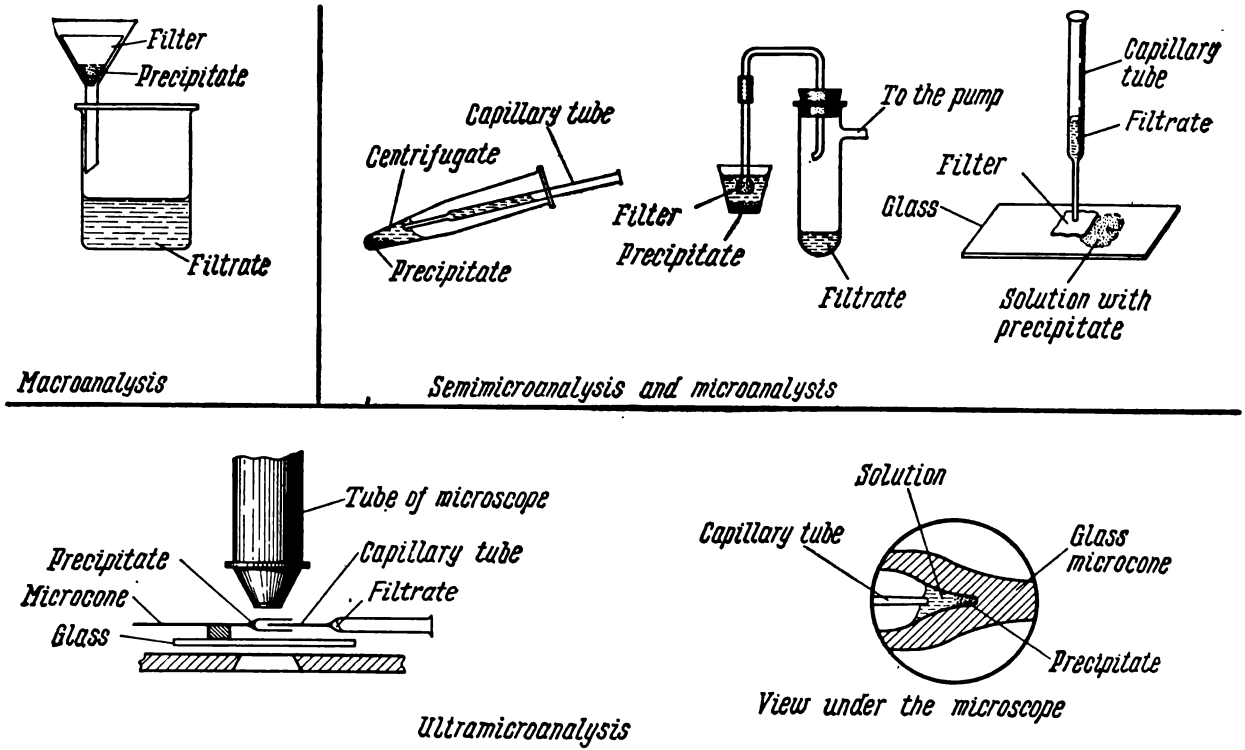


Fig. II-3. Separation of the precipitate from the solution in various methods of analysis

Microanalysis. A porcelain plate for spot reactions, a washer with a capacity of 5-10 ml, a microcrucible, and a microscope slide for microcrystalloscopic reactions.

Ultramicroanalysis. A microscope with manipulators (see Fig. I-6) and a set of microcones.

An illustration with a graphic representation of operations (filtration, for example) in different methods of analysis may be presented (Fig. II-3).

CHARACTERISTICS OF ANALYTICAL REACTIONS

Qualitative chemical analysis is largely based on reactions which are accompanied with a characteristic external effect. At that, the qualitative aspect of a chemical process and the stoichiometric relationship of elements entering the composition of the compounds being formed are not very important. Two features of chemical reactions are important: sensitivity and selectivity.

Sensitivity of Reactions

The sensitivity of a reaction is expressed by the value of the limit of detection (ppm, μg/ml, etc.). Sensitivity is expressed also in percentage. For colour reactions, the criterion of sensitivity may be the molar absorptivity $\bar{\varepsilon}$.

The sensitivity of a reaction may be increased by changing the concentration of reagents, the pH of the medium, and the order in which reagents are mixed, by extraction, flotation, coprecipitation, and the formation of mixed complex compounds, and also by using different methods of carrying out reactions (spot test analysis, pyrochemical analysis, and so forth) and the methods of observing reaction products (in an ordinary light microscope or electron microscope, in an ultraviolet light, and so forth). The limits of detection for different methods of qualitative analysis are given below (in percentage) [1]:

Pyrochemical	10^{-3}—10^{-4}
Spot tests	10^{-4}—10^{-5}
Microcrystalloscopic	10^{-4}—10^{-5}
Spectrographic	10^{-4}—10^{-6}
Luminescence	10^{-5}—10^{-7}
Catalytic	10^{-7}—10^{-9}
Mass spectrometric	10^{-8}—10^{-9}
Neutron activation	10^{-7}—10^{-12}

Comparison of the Sensitivity of Reactions

Experiment 1. Comparison of Colour Intensity of Copper Complexes

Many copper (II) complexes, being charge-transfer complexes, have intensive absorption bands. The intensity and position of the absorption band (wavelength) change in conformity with the ligand field strength. The stability of the complex also changes. This accounts for the difference in the sensitivity of the reaction of the copper ion with different reagents (Table II-1):

$$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftarrows [CuCl_4]^{2-} + 6H_2O$$

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftarrows [Cu(NH_3)_4]^{2+} + 6H_2O$$

$$2[Cu(H_2O)_6]^{2+} + [Fe(CN)_6]^{4-} \rightleftarrows Cu_2[Fe(CN)_6]\downarrow + 12H_2O$$

Table II-1

SENSITIVITY OF REACTIONS OF THE CUPRIC ION WITH DIFFERENT REAGENTS

Complex	log β_n *	Colour of complex	Limit of detection, ppm
$[CuCl_4]^{2-}$	0.01 (20 °C, $\mu = 0.7$)	Yellow-green	20
$[Cu(NH_3)_4]^{2+}$	12.56 (18° C. $\mu \to 0$)	Blue	4
$Cu_2[Fe(CN)_6]$	15.68 ** (25° C, $\mu \to 0$)	Red-brown	0.4

* β_n-overall stability constant,
** The value of $-\log K_{sp}$ (solubility product) is given.

Reagents

Cupric sulphate, 1 per cent solution.
Ammonia, 25 per cent solution.
Hydrochloric acid, concentrated.
Potassium ferrocyanide, 10 per cent solution.

Procedure. In one cylinder, put 40 ml of copper sulphate solution and 300 ml of water, in another, 30 ml of copper sulphate solution and 400 ml of water, and in the third, 20 ml of copper sulphate solution and 450 ml of water. At the lecture, add 150 ml of hydrochloric acid solution to the first cylinder; a yellow-green colour appears. To the second

cylinder, add 50 ml of ammonia solution; a blue colour appears. To the third, add 20 ml of potassium ferrocyanide solution; a red-brown precipitate appears.

Note. Draw the attention of the audience to the decrease in the amount of the reagent that is necessary for the formation of a compound and to the greater intensity of colour when more stable complexes are formed.

Experiment 2. Comparison of Colour Intensity of Iron (III) Complexes

The intense colour of complexes of the ferric ion with the halide and thiocyanate ions is due to the charge transfer band in the visible and ultraviolet regions of the spectrum. The degree of charge transfer and, consequently, the colour intensity of the aqueous solutions of complexes increase in the order $NCS^- > Br^- > Cl^-$ (Table II-2).

Table II-2

SENSITIVITY OF REACTIONS OF THE FERRIC ION WITH DIFFERENT REAGENTS

Complex	$\log \beta_i$	Colour of complex	Limit of detection, ppm
$[FeCl_4]^-$	1.48 (25° C, $\mu \to 0$)	Yellow-green	10
$[FeBr_4]^-$	0.49 (20° C, $\mu \to 0$)	Dark yellow	1
$[Fe(NCS)_4]^-$	1.96 (18° C, $\mu = 1.8$)	Red	0.05

Hence, iron complexes behave in a similar way as copper complexes, and the afore-mentioned statement is valid for them (see previous experiment):

$$[Fe(H_2O)_6]^{3+} + 4Cl^- \rightleftarrows [FeCl_4]^- + 6H_2O$$

$$[Fe(H_2O)_6]^{3+} + 4Br^- \rightleftarrows [FeBr_4]^- + 6H_2O$$

$$[Fe(H_2O)_6]^{3+} + 4NCS^- \rightleftarrows [Fe(NCS)_4(H_2O)_2]^- + 4H_2O$$

Reagents

Ferric chloride, 1 per cent solution in 1 *M* solution of hydrochloric acid.

Hydrochloric acid, concentrated.

Potassium bromide, saturated solution.

Ammonium thiocyanate, 5 per cent solution.

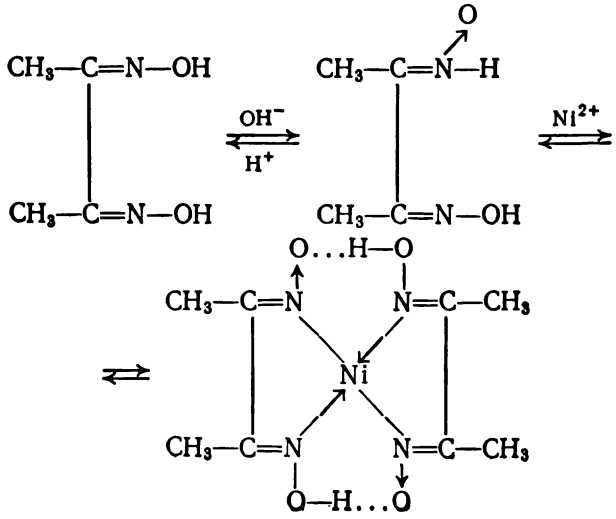
Procedure. Take three cylinders and in each of them put 20 ml of iron chloride solution; then, into the first cylinder pour 100 ml of water, into the second, 50 ml of water, and into the third, 200 ml of water. At the lecture, add 100 ml of concentrated hydrochloric acid to the first cylinder; a yellow-green colour appears. Add 150 ml of potassium bromide solution to the second cylinder; a dark yellow colour appears. Add 20 ml of ammonium thiocyanate solution to the third cylinder; an intense red colour appears.

Experiment 3. Determination of the Sensitivity of Reactions by Diluting a Solution

The limit of detection of many colour reactions may be established experimentally, for instance, by diluting the solution of a substance being studied.

Variant 1. A Decrease in the Amount of Nickel Dimethylglyoximate when a Nickel Salt Solution Is Diluted

Nickelous ions with dimethylglyoxime form a chelate compound of pink colour. Dimethylglyoxime at first undergoes a tautomeric transformation, producing a form in which the hydrogen ion is easily replaced by a metal ion [2]:



The reaction between the nickel ion and dimethylglyoxime is very sensitive: limit of detection equals 3.3 ppm.

Reagents
Nickelous sulphate, 1 per cent solution.
Dimethylglyoxime, 1 per cent ethanol solution.

Procedure. Place three cylinders on the demonstration table. In one of them, put 20 ml of nickel sulphate solution and 300 ml of water. At the lecture, pour 20 ml of this solution into another cylinder, add 300 ml of water and stir. Pour 20 ml of the solution obtained into the third cylinder and add 300 ml of water. To each of the cylinders, add 50 ml of dimethylglyoxime solution. A pink precipitate appears everywhere. Its amount diminishes from the first to the last cylinder.

Variant 2. A Decrease in the Colour Intensity of Copper Ammoniate when a Copper Salt Solution Is Diluted

For the reaction of cupric ion with ammonia, the limit of detection is 4 ppm.

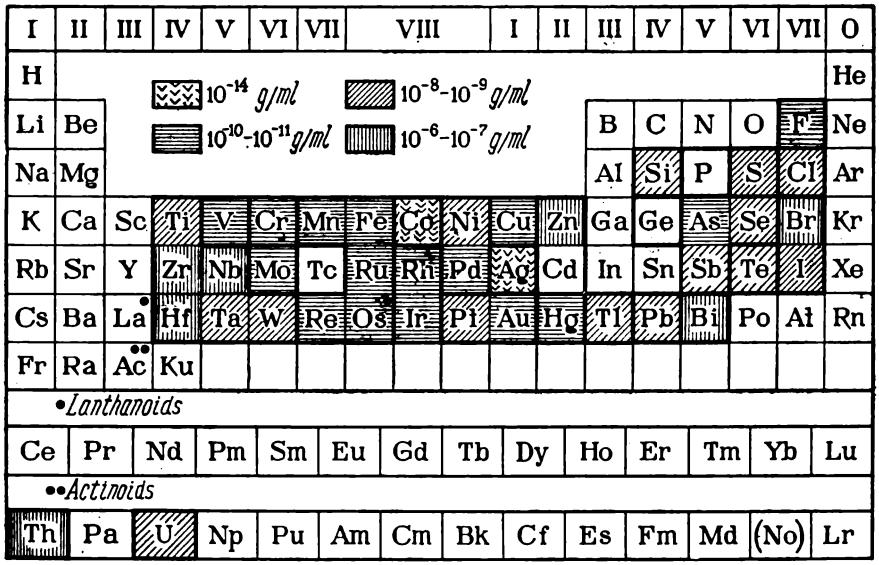
Reagents
Cupric sulphate, 1 per cent solution.
Ammonia, 25 per cent solution.

Procedure. Place three cylinders on the table. In one of them, put 25 ml of copper sulphate solution and 300 ml of water. At the lecture, pour 20 ml of this solution into another cylinder, add 300 ml of water and stir. Pour 20 ml of the solution obtained into the third cylinder, add 300 ml of water and stir. To each of the cylinders, add 50 ml of ammonia solution. Colour intensity decreases from the first to the last cylinder.

Note. Apart from the afore-mentioned reactions, use may be made of many reactions which are accompanied with the formation of a coloured precipitate or a complex compound, such as reactions of the ferric ion with sulphosalicylic acid or potassium ferrocyanide.

High-Sensitive Catalytic Reactions for Detecting Elements

Catalytic reactions may be successfully used for detecting element traces, since even inconsiderable amounts of elements (catalysts) accelerate many chemical reactions [3]. The sensitivity of element determination with the utilization of catalytic reactions is given below in the Mendeleev table.


10^{-14} g/ml
10^{-8}-10^{-9} g/ml
10^{-10}-10^{-11} g/ml
10^{-6}-10^{-7} g/ml
I II III IV V VI VII VIII I II III IV V VI VII 0
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Ac Ku
•Lanthanoids
Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
••Actinoids
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md (No) Lr

Experiment 4. Catalytic Reaction for Detecting the Palladium Ion

Sodium hypophosphite slowly reduces the nickel ion to metal; the presence of extremely small amounts of palladium ions and also salts of other platinum metals (1.5 μg Pt; 0.5 μg Os; 0.5 μg Ru) accelerates a reaction.

$$2Ni^{2+} + H_2PO_2^- + 2H_2O \longrightarrow 2Ni\downarrow + H_2PO_4^- + 4H^+$$

The limit of detection is 0.0025 ppm. The catalytic action of palladium (II) is probably due to intermediate reactions, including the formation of metallic palladium in a colloidal state owing to reduction by sodium hypophos-

phite and the decomposition of sodium hypophosphite with hydrogen liberation [4].

Reagents

Nickelous acetate, 1 per cent solution.
Sodium hypophosphite, saturated solution.
Palladium chloride, 0.001 per cent solution in 1 *M* *hydrochloric acid solution.*

Procedure. Take two 0.5-litre beakers which are carefully washed and rinsed with alcohol and ether, and in each of them put 150 ml of nickel acetate solution. At the lecture, add 15 ml of sodium hypophosphite solution to each beaker. No change is observed. Add 10 ml of palladium chloride solution to one beaker. Heat both beakers. In several minutes, there is a rapid liberation of hydrogen and metal nickel in the form of a mirror on the walls of the vessel and in the form of black powder from the solution containing palladium ions. In the second beaker, the solution remains green, and metal nickel is separated only after long heating.

Experiment 5. Catalytic Reaction for Detecting Cobalt Traces

Alizarin, which has a violet colour in an alkaline solution, is oxidized by hydrogen peroxide prior to the formation of colourless products. The reaction is accelerated in the presence of very small amounts of cobalt ions (up to 0.05 ppm) [5].

The mechanism of catalytic action may be explained in the following way. A cobaltous ion in an alkaline medium forms a complex ion with hydrogen peroxide:

$$[CoOH]^+ + H_2O_2 \rightleftarrows \left| Co\begin{matrix} OH \\ O_2H_2 \end{matrix} \right|^+$$

The complex being formed decomposes with the formation of a hydroxyl radical ·OH and a cobaltic ion

$$\left[Co\begin{matrix} OH \\ O_2H_2 \end{matrix} \right]^+ \rightleftarrows [Co(OH)_2]^+ + \cdot OH$$

Catalyst regeneration occurs according to the pattern:

$$[Co(OH)_2]^+ + O_2H^- \rightleftarrows [Co(OH)]^+ + \cdot O_2H + OH^-$$

The hydroperoxide radical $\cdot O_2H$ being formed and the hydroxyl radical $\cdot OH$ oxidize alizarin to the derivatives of acrylic acid.

Reagents

Cobaltous sulphate, solution corresponding to a cobalt concentration of 1 mg/ml.

Alizarin S, 0.01 per cent solution. 0.01 g of a reagent is dissolved in 100 ml of water, and 3 ml of 0.01 *N* sodium hydroxide solution are added.

Hydrogen peroxide, 3 per cent solution.

Borate buffer solution. 19 g of sodium tetraborate decahydrate are dissolved in 1 litre of water.

Sodium hydroxide, 30 per cent solution.

Procedure. In a cylinder, put 2 ml of cobalt sulphate solution and 400 ml of water, and in another, 400 ml of water. At the lecture, add to each cylinder 20 ml of sodium hydroxide solution, 50 ml of buffer solution, 20 ml of hydrogen peroxide solution, and 20 ml of Alizarin S solution. A violet colour appears. In the cylinder with cobalt sulphate, the colour fades and disappears in 10-20 minutes, while in the cylinder with water, the colour keeps for a long time.

Note. The time of decoloration of Alizarin S by hydrogen peroxide in the absence of cobalt ions depends on the purity of the reagents.

Increase in the Sensitivity of a Reaction by Solvent Extraction

The extraction of a compound from a solvent, which is usually water, into another one often makes it possible to increase sensitivity in detecting an element. An increase in sensitivity is due, on the one hand, to a growth in the concentration of the substance being analyzed (on extraction from a larger volume into a smaller one) and, on the other, to the polarizing action of the solvent, which leads to a change in colour intensity and sometimes in the colour itself of the compound being extracted.

Experiment 6. Extraction of Iron Thiocyanate

A ferric ion forms with thiocyanate ions several complex ions of red colour, depending on the ligand concentration. The acido complexes formed are extracted by organic polar solvents according to the hydrate-solvate mechanism [6]

$$[Fe(NCS)_n(H_2O)_{6-n}]_{aq}^{(n-3)-} + (n-3)H_{aq}^{+} + mH_2O + lS_{org} \rightleftarrows H_{n-3}(H_2O)_mS_l[Fe(NCS)_n(H_2O)_{6-n}]_{org}$$

An increase in the sensitivity of detecting iron in this case is due to a growth in concentration as a result of the transfer of the complex from a larger volume to a smaller one. The sensitivity of the reaction m is 5 μg in 10 ml of a non-aqueous solvent on extraction from 50 ml of an aqueous solution [7].

Reagents

Ferric chloride, 0.1 per cent solution in 0.1 *N* hydrochloric acid solution.
Hydrochloric acid, concentrated.
Ammonium thiocyanate, 10 per cent solution.
Mixture of isoamyl alcohol and benzene (4 : 1).

Procedure. In a cylinder, put 2 ml of iron chloride solution, 10 ml of concentrated hydrochloric acid and 400 ml of water. At the lecture, add 50 ml of ammonium thiocyanate solution and stir. The colour is almost unnoticeable. Add 100 ml of a solvent mixture and shake several times (use a protective screen!). The formation of two phases is observed: a colourless aqueous phase and an organic phase of red colour.

Note. Phases are separated better when the solvent mixture is used.

Experiment 7. Extraction of Iodine by Chloroform

An example of increasing the sensitivity in the case of a change in the polarizing action of a solvent is extraction of iodine by organic solvents. Iodine dissolves poorly in water, but well in organic solvents (polar and nonpolar). The colour of an iodine solution depends on the nature of a solvent [8]. In donor solvents, there occurs

solvation and the formation of charge-transfer complexes of the type $I_2 \ldots S$, where S is water, alcohol, benzene, and so forth. The charge transfer is effected either from a π-electron system of a benzene molecule or from a free pair of electrons of the molecules of ethers, alcohols, amines. This causes the appearance of a characteristic yellow-brown colour. In such solvents as carbon tetrachloride and chloroform, iodine in not solvated and has its own violet colour.

Reagents

Iodine, 1 per cent solution. One gram of iodine and four grams of potassium iodide are dissolved in 100 ml of water.

Chloroform.

Procedure. In a cylinder, put 10 ml of iodine solution and 200 ml of water. The solution has a faint yellow colour. At the lecture, add 70 ml of chloroform and shake. The formation of two phases is observed: a colourless aqueous phase and a violet organic phase (against a white screen).

Increase in the Sensitivity of a Reaction by Introducing Water-Miscible Organic Solvents

The sensitivity of some reactions is increased by introducing water-miscible organic solvents (acetone, dioxane). In this case, the dielectric constant of the medium and the degree of dissociation of a compound decrease. When the formation of complexes is stepwise, they may be formed with a large number of ligands; this also increases colour intensity and, consequently, the sensitivity of a reaction. The introduction of organic solvents promotes also the dehydration of the aquo ions of metals.

Experiment 8. Formation of Iron Thiocyanate in the Presence of Acetone

The iron (III) thiocyanate complex is a charge-transfer complex; this explains its intense red colour. Colour intensity grows with an increase in the number of ligands around iron (III) due to the greater probability of the

transition of electrons from the thiocyanate ion to the iron ion. The apparent molar absorptivity $\bar{\varepsilon}$ of the bis-complex is approximately twice as high as that of the mono-complex. On a decrease in the dielectric constant of the medium, for example, on an addition of acetone to water, equilibrium is displaced towards the formation of higher complexes; this intensifies colour: when $\lambda = 480$ nm in an aqueous solution $\bar{\varepsilon} = 7 \cdot 10^3$, and in a water-acetone mixture [9], $\bar{\varepsilon} = 1.5 \cdot 10^4$.

Reagents

Ferric chloride, 0.1 per cent solution in 0.1 *N* hydrochloric acid solution.
Ammonium thiocyanate, 10 per cent solution.
Acetone.
Hydrochloric acid, concentrated.

Procedure. In a cylinder, put 10 ml of iron chloride solution, 10 ml of hydrochloric acid and 300 ml of water. At the lecture, add 40 ml of ammonium thiocyanate solution. Separate the red solution obtained into two parts. To one part, add 150 ml of acetone, and to the other, 150 ml of water. It may be seen that the colour in the first cylinder is more intense than that in the second one (use a white screen!).

Increase in the Sensitivity of a Reaction by Flotation

One of the ways of increasing the sensitivity is by concentrating a substance at the interface of two immiscible liquids (flotation).

Experiment 9. Flotation of Nickel Dimethylglyoximate

Nickel dimethylglyoximate cannot be extracted from an aqueous solution by such organic solvents as ethers and alcohols, although the complex contains two hydroxyl groups and two hydrogen atoms, which could easily solvate. However, solvation does not occur, since these groups are linked by a strong internal hydrogen bond. The presence of a non-polar hydrophobic part in a molecule of nickel dimethylglyoximate promotes the accumulation of the complex in the surface layer owing to the ex-

truding action of water (flotation effect) (see Chapter VII, p. 158).

Reagents

Nickelous sulphate, solution corresponding to a nickel concentration of 20 μg/ml.
Dimethylglyoxime, 1 per cent ethanol solution.
Diethyl ether.
Ammonia, 25 per cent solution.

Procedure. In a cylinder, put 3 ml of nickel sulphate solution and 400 ml of water. At the lecture, add 50 ml of dimethylglyoxime solution and 5 ml of ammonia solution. The colour of the complex is almost unnoticeable (the solution is slightly yellowish). Add 100 ml of diethyl ether and strongly shake the cylinder several times (use a protective screen!). Put the cylinder against a white screen and observe the formation of a pink film known as "Langmuir's palisade" at the interface.

Note. For the lecture experiment to be successful, the amount of nickelous sulphate must be accurately measured. When the concentration is too high, the nickel dimethylglyoximate film creeps along the wall of the cylinder and outwardly produces the effect of extraction. When the concentration is too low, the film does not form immediately.

Increase in the Sensitivity of a Reaction by Forming Mixed Complexes

Experiment 10. Formation of a Molybdovanadophosphoric Heteropoly Acid

The phosphate ion forms, together with the molybdate ion, a molybdophosphoric acid of yellow colour by the pattern:

$$H_2PO_4^- + 12MoO_4^{2-} + 25H^+ \rightleftarrows H_3[PMo_{12}O_{40}] + 12H_2O$$

The reaction is low-sensitive, and the molar absorptivity $\bar{\varepsilon}$ is 600 when $\lambda = 400$ nm. The introduction of a third component [vanadium (V), iron (III), bismuth (III)] into the heteropoly complex increases the sensitivity of the reaction by several times. For example, the molar absorpti-

vity $\bar{\varepsilon}$ of molybdovanadophosphoric acid is $2.5 \cdot 10^3$ when $\lambda = 400$ nm [9].

Reagents

Potassium dihydrophosphate, 0.5 per cent solution.
Sodium molybdate, 10 per cent solution.
Ammonium vanadate, 2.5 per cent solution.
Sulphuric acid, 1 *M* solution.

Procedure. In a cylinder, put 20 ml of potassium dihydrophosphate solution, 100 ml of sulphuric acid solution and 400 ml of water. At the lecture, separate the solution into two parts. To one part, add 50 ml of sodium molybdate solution. A faint yellow colour of a double heteropoly complex appears. To the second part, add 50 ml of ammonium vanadate solution and 50 ml of sodium molybdate solution. An intense yellow-orange colour of the ternary complex appears.

Increase in the Sensitivity of a Reaction by the Multiplication Method

One of the ways of increasing the sensitivity of determination is by using the so-called "multiplication" reactions (the multiplication method). The method consists in the conduction of a series of consecutive reactions as a result of which a substance is produced in an amount that is several times greater than the initial content of the substance being analyzed in the test (multiplication). The method is usually used for quantitative determinations.

Here are patterns of some multiplication reactions in which the ions being determined are framed [10] (multiplication factors are given in brackets):

$$AgIO_3 + \boxed{Cl^-} \longrightarrow AgCl + IO_3^- \xrightarrow{I^-} 3I_2 \qquad (3)$$

$$2AgI + \boxed{S^{2-}} \longrightarrow Ag_2S + 2I^- \longrightarrow 2IO_3^- \xrightarrow{I^-} 6I_2 \qquad (6)$$

$$\boxed{Me^{n+}} + \underset{\text{excess}}{H_2Y^{2-}} \longrightarrow [MeY]^{(n-4)+} + H_2Y^{2-} +$$

$$+ Pb(IO_3)_2 \longrightarrow 2IO_3^- \xrightarrow{I^-} 6I_2 \qquad (6)$$

where Me = Pb, Hg, Bi, Cu, Cd, Ni, Co, Zn, Fe, Al, In, Th.

H_2Y^{2-} = EDTA anion.

$$Ba(IO_3)_2 + \boxed{SO_4^{2-}} \longrightarrow BaSO_4 + 2IO_3^- \xrightarrow{I^-} 6I_2 \qquad (6)$$

$$\boxed{PO_4^{3-}} + 12MoO_4^{2-} \longrightarrow [PMo_{12}O_{40}]^{3-} \xrightarrow{Pb^{2+}} 12PbMoO_4 \qquad (12)$$

Experiment 11. Detection of the Iodide Ion by the Multiplication Method

For determining iodide, it is oxidized to iodate by strong oxidizing agents (for example, potassium permanganate, potassium periodate, and halogens in an alkaline medium) [11]:

$$I^- + 3IO_4^- \rightleftarrows 4IO_3^-$$

$$2MnO_4^- + I^- + 3H_2O \rightleftarrows 2MnO(OH)_2 + 2OH^- + IO_3^-$$

Potassium iodide is added after the excess of the oxidizing agent is removed. In this case, iodine is obtained in the amount that is six times greater than the amount of iodine present in the form of iodide in the stock solution.

Iodine which is obtained may be distilled off; then, again it may be oxidized to an iodate ion and acidified, iodide may be added and thus free iodine obtained in an amount that is already 36 times greater than the initial content of iodine in the sample, and so forth.

The multiplication method makes it possible to determine up to 1 μg of iodine in 100 ml of the solution being analyzed.

Reagents

Potassium iodide, 5 per cent and 0.01 per cent solutions.
Potassium hydroxide, 7 *M* solution.
Potassium permanganate, 0.05 *N* solution.
Oxalic acid, 0.1 *N* solution.
Acetic acid, 10 *M* solution.
Sulphuric acid, 1 *M* solution.
Potassium iodate, 0.5 per cent solution.

Procedure. In a 1-litre beaker, put 50 ml of 0.01 per cent potassium iodide solution and 500 ml of water. At the

lecture, separate the solution into two parts. To one part, add 20 ml of sulphuric acid solution and 20 ml of potassium iodate solution. A scarcely noticeable yellowing of the solution is observed. To the other part, add 20 ml of potassium hydroxide solution, heat to boiling, add 15 ml of potassium permanganate solution, boil for one minute, and then, to destroy the excess permanganate ion, add 10 ml of oxalic acid solution and 20 ml of acetic acid solution. On cooling, add 20 ml of 5 per cent potassium iodide solution and 50 ml of sulphuric acid solution. A more intense colour of the iodine solution is observed.

Note. In using potassium periodate as an oxidizing agent, its excess is removed by precipitation in an ammonia buffer solution in the form of $Zn_5(IO_6)_2$ or from a weak acid solution in the form of $Hg_5(IO_6)_2$.

Selectivity and Specificity of Reactions

In the main, qualitative analysis deals with selective reactions. Selectivity is determined by the characteristics of a reagent and the metal ion and by the conditions under which a reaction is carried out (medium, the presence of masking agents).

The influence of foreign ions is quantitatively estimated by the *limiting proportion* (*LP*):

$$LP = \frac{g \text{ of the ion being determined}}{g \text{ of a foreign ion}}$$

where g = mass.

Reactions or reagents that yield products with characteristic properties only with one type of ions are called specific. Such reactions are very few.

Experiment 12. Selective Detection of Metal Ions in the Form of Sulphides

A doubly-charged sulphur anion S^{2-} is so great (r = = 1.74 Å) that it is easily polarized with cations, forming a covalent bond, especially if the cations themselves are easily deformed. The formation of a covalent bond is promoted by the low energy of vacant 3*d*-orbitals of sul-

phur, as a result of which some "back bonding" is possible by transferring electrons from atoms of a metal with filled or almost filled *d*-orbitals to these orbitals. Therefore, for metals with *d*-electrons, a considerable splitting of energy levels formed by *d*-orbitals is observed; this leads to an intensive colouring of most sulphides. In the case of the same electron structure of ions, the colour deepens as their ionic radius increases. For example, the difference in the colour of zinc sulphides and cadmium sulphides is due to the greater radius of cadmium. Here, it is expedient to demonstrate a table showing the connection of the electron structure of a metal ion and the ionic radius with sulphide colour (Table II-3).

Table II-3

COLOUR OF METAL SULPHIDES AS DEPENDENT ON THE STRUCTURE AND RADIUS OF IONS

Ion	Outer electron shell	r_i, Å	Sulphide colour
Zn^{2+}	$3d^{10}$	0.83	White
Mn^{2+}	$3d^{5}$	0.91	Pink
Cd^{2+}	$4d^{10}$	1.03	Yellow
Sb^{III}	$4d^{10}5s^{2}$	0.90	Orange
Cu^{2+}	$3d^{9}$	0.80	Black

Reagents

Chlorides of zinc, cadmium, antimony (III), copper (II) and manganese (II), 1 per cent solutions.
Hydrochloric acid, 6 *M* solution.
Hydrogen sulphide, saturated solution.

Procedure. Take four cylinders and in each of them put 50 ml of salt solutions and 300 ml of water. Create the necessary medium by adding ammonia or hydrochloric acid (pH = 2 in a zinc salt solution, pH = 1 in cadmium and copper salt solutions, and 2 *M* according to hydrochloric acid in an antimony salt solution). At the lecture, add to every cylinder 20-30 ml of hydrogen sulphide solution. This results in the formation of white zinc sulphide, yellow cadmium sulphide, orange antimony sulphide and black copper sulphide.

By using the characteristic colour of metal sulphides and varying the conditions of reaction (pH, masking agents), it is possible to selectively detect some elements, such as antimony in the presence of manganese, zinc, cadmium.

In a cylinder, mix beforehand 20 ml of manganese chloride solution, 20 ml of zinc chloride solution, 20 ml of cadmium chloride solution and 20 ml of antimony chloride solution, and add 50 ml of hydrochloric acid solution and 200 ml of water. At the lecture, add 30 ml of hydrogen sulphide water. An orange precipitate of antimony sulphide is formed.

Note. Sulphide precipitates may be obtained beforehand and cylinders may be put on the demonstration table, attaching labels with the formulas of metal sulphides to them. Other sulphides (pink manganese sulphide, yellow arsenic sulphide) may also be obtained.

Experiment 13. Selective Reaction Between the Nickel Ion and Dimethylglyoxime

The formation of a chelate compound of nickel (II) with dimethylglyoxime $Ni(DH)_2$ of pink colour in an ammonia medium (pH = 8) is a selective reaction in analytical chemistry (see Experiment 3):

$$\log \beta_2 = 17.72 \ (25^\circ C, \ \mu \to 0)$$
$$-\log K_{sp} = 23.37 \ (25^\circ C, \ \mu = 0.05)$$

Only some cations, Fe^{2+}, Co^{2+}, Cu^{2+}, Pd^{II}, Pt^{II}, Bi^{III}, Re^{VII}, react with dimethylglyoxime. However, the conditions of reactions are different. For example, palladium dimethylglyoximate is formed in an acid medium, and cobalt dimethylglyoximate is formed when concentrations are large ($LP = g_{Ni}/g_{Co} = 1 : 5000$). In an ammonia-tartrate buffer solution, ferrous dimethylglyoximate is not formed in the presence of an oxidizing agent. Having selected the conditions, the nickel ion may be detected in the presence of almost all cations.

Reagents

Chlorides of nickel (II), cobalt (II), zinc, chromium (III), aluminium and iron (III), 1 per cent solutions, in 0.1 *N* hydrochloric acid solution.

Dimethylglyoxime, 1 per cent ethanol solution.
Ammonia-tartrate buffer solution. To 100 ml of saturated potassium tartrate solution, add 20 ml of 25 per cent ammonia solution.

Procedure. In a cylinder, put 4 ml of cobalt chloride solution, 4 ml of zinc chloride solution, 4 ml of chromium chloride solution, 4 ml of aluminium chloride solution, 4 ml of iron chloride solution and 400 ml of water. At the lecture, add 100 ml of buffer solution and pour the solution into two cylinders. To the first cylinder, add 20 ml of nickel chloride solution, and into each of the two cylinders pour 50 ml of dimethylglyoxime solution. In the first cylinder, a bulky pink precipitate of nickel dimethylglyoximate is formed, and in the second, no precipitate is formed.

Note. The experiment is also a demonstration of the masking influence of tartrate ions, which is used for increasing the selectivity of a reagent [masking of chromic and ferric ions].

Experiment 14. Specific Reaction for Detecting Ammonium Ions

The reaction of separating ammonia from ammonia salts upon interaction with alkalies is specific. Ammonia may also be detected by a change in the pH of the medium and by the formation of a characteristic compound of ammonium chloride:

$$NH_4^+ + OH^- \rightleftarrows NH_3\uparrow + H_2O$$

$$NH_3 + HCl \rightleftarrows NH_4Cl$$

Reagents
Ammonium chloride.
Ammonium nitrate.
Sodium chloride.
Sodium hydroxide, 20 per cent solution.
Hydrochloric acid, concentrated.
Phenolphthalein, 0.1 per cent ethanol solution.

Procedure. *Variant 1.* Take three vessels and put one gram of ammonium chloride into one vessel, one gram of ammonium nitrate into another vessel, and one gram of

sodium chloride into the third vessel. Suspend strips of filter paper impregnated with a phenolphthalein solution and wetted with water so that they do not touch the salts (Fig. II-4). Take a pipette and add an alkaline solution to every vessel, not touching the strips of paper. In the first two vessels, the reddening of the paper is observed; in the vessel with sodium chloride, the paper remains colourless.

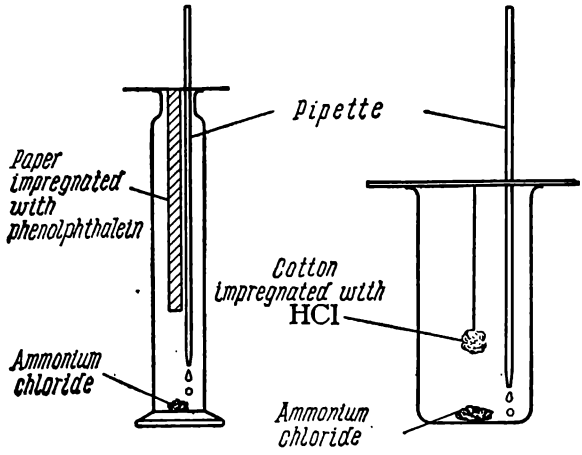


Fig. II-4. Instruments for demonstrating reactions of detecting the ammonium ion

Variant 2. Take three vessels and put one gram of ammonium chloride into one vessel, one gram of ammonium nitrate into another vessel, and one gram of sodium chloride into the third vessel. On strings, suspend pieces of cotton wetted with a concentrated hydrochloric acid solution (Fig. II-4). To every vessel, add an alkaline solution, not touching the cotton with the pipette. In the first two vessels, thick white smoke of ammonium chloride appears; in the third cylinder, there is no smoke.

METHODS OF QUALITATIVE ANALYSIS

Microcrystalloscopic Analysis

For detecting cations and anions, use may be made of reactions which result in the formation of compounds with a characteristic crystal shape. The form and rate of cry-

stallization are influenced by the conditions of a reaction. A significant role in microcrystalloscopic reactions is

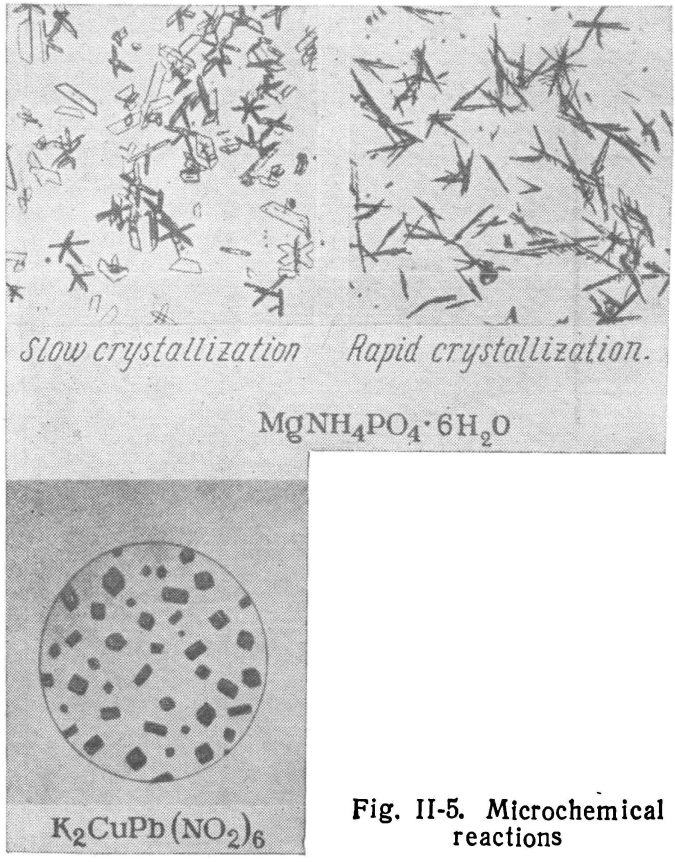


Fig. II-5. Microchemical reactions

Table II-4

SENSITIVITY OF MICROCRYSTALLOSCOPIC REACTIONS

Ion	Compound being precipitated	Limit of detection, ppm
Co^{2+}	$Co[Hg(SCN)_4]$	100
Zn^{2+}	$Zn[Hg(SCN)_4]$	50
Pb^{2+}	PbI_2	35
Pb^{2+}	$K_2Pb[Cu(NO_2)_6]$	15
Bi^{3+}	$Cs[BiI_4]$	50

played by the evaporation of a solvent, leading to a more concentrated solution and, consequently, to an increase in the sensitivity of determining the ion (Table II-4) [12].

At the lecture, illustrations of characteristic crystals of some compounds used for detecting ions (Fig. II-5) may be presented. When the appropriate projectors are available, the formation and growth of crystals may be demonstrated to the audience [13].

Pyrochemical Analysis

On heating substances in a burner flame, different characteristic phenomena may be observed: sublimation, evaporation, melting, colour change, flame coloration, and so forth. All these phenomena are used in qualitative analysis for preliminary tests of substances. Sometimes, pyrochemical reactions may be used to increase the selectivity and sensitivity of determination. Pyrochemical reactions are used for analyzing minerals in field conditions.

Flame Coloration

When a metal salt solution is put into a flame, several complex processes occur: evaporation, the formation of solid aerosols, dissociation, ionization, interaction with oxygen, and the excitation of atoms, ions and molecules. The outcome of these processes is an analytically used effect: flame glow [14, 15].

Experiment 15. Flame Coloration by the Salts of Alkali and Alkali-Earth Metals

For alkali metals, use is made of the atomic resonance lines of transitions $n^2S_{1/2}$-$n^2P^0_{1/2,\ 3/2}$, for alkali-earth metals, the atomic resonance lines $n^1S_0 - n^1P^0$, and for calcium and strontium, the bright molecular bands caused by such molecules as MeO and MeOH. It is expedient to show the audience a table of spectral analytical lines and the appropriate electron transitions [14] (Table II-5).

Reagents

Chlorides of alkali and alkali-earth metals, salts or their saturated solutions.

Table II-5

SPECTRAL ANALYTICAL LINES OF ALKALI AND ALKALI-EARTH ELEMENTS

Elements and compounds	Transition	Spectral lines (wavelength, nm)	Flame colour
Lithium	$n^2S_{1/2} - n^2P^\circ_{3/2}$	670.8	Crimson
Sodium	$n^2S_{1/2} - n^2P^\circ_{1/2,\,3/2}$	589.6 and 589.0	Yellow
Potassium	$n^2S_{1/2} - n^2P^\circ_{1/2,\,1/2}$	769.9 and 766.5	Violet
Barium	$n^1S_0 - n^1P^\circ$	535.5	Green
Strontium	$n^1S_0 - n^1P^\circ$	460.7	Carmine red
SrO, SrOH		610 and 670	
Calcium	$n^1S_0 - n^1P^\circ$	422.7	Brick red
CaO, CaOH		554 and 622	

Procedure. Treat beforehand a platinum or nichrome wire with concentrated hydrochloric acid and roast it in a burner flame until the yellow colour of the flame disap-

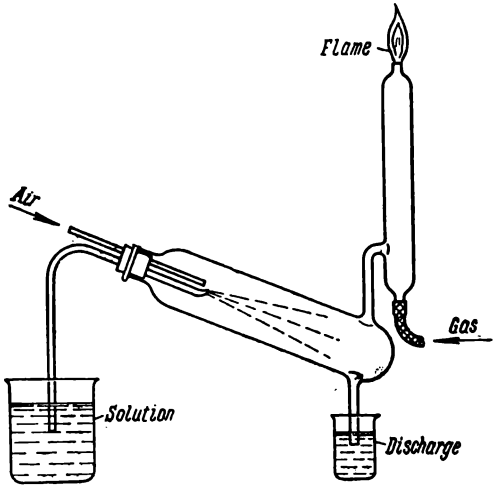


Fig. II-6. Diagram of a sprayer for flame photometry

pears. At the lecture, put the end of a platinum or nichrome wire with salt grains into a burner flame. The end of a wire with an eye to which a piece of filter paper wetted with a solution of the appropriate salt is fastened

may be put into the flame. Moreover, it is possible to introduce a salt solution in the form of aerosols, employing a special sprayer (Fig. II-6).

Note. Draw the listeners' attention to the fact that sodium compounds are present everywhere; for example, the sweat glands of a human being excrete sodium chloride. Therefore, if a clean wire is rubbed with the fingers and put into a burner flame, the flame becomes bright yellow. Moreover, hands may be clapped in front of a burner.

Experiment 16. Flame Coloration by Boron Compounds

When boric acid or other boric compounds are put into the flame, a characteristic green colour (spectral lines in the range of 460-640 nm) originates. Owing to the high thermal stability of boron oxides, the atomic lines of boron are not observed in the flame spectrum, and the green colour is due to the excitation of the boron oxide B_xO_y or BO_2 in the flame. Organic boron compounds (for example methyl ether of boric acid) are highly volatile; therefore, the introduction of boron into the flame in the form of an organic compound creates a considerable concentration of molecules of gaseous boron oxides, and the intensity of radiation grows accordingly 10-17 times). The sensitivity of detecting boron in the form of methyl ether of boric acid is 1.7 μg/ml:

$$B(OH)_3 + 3CH_3OH \rightleftarrows B(OCH_3)_3 + 3H_2O$$

$$2B(OCH_3)_3 + 9O_2 \longrightarrow B_2O_3 + 9H_2O + 6CO_2\uparrow$$

Reagents
Boric acid or its salts.
Methanol or ethanol.
Sulphuric acid, concentrated.

Procedure. *Variant 1.* In a porcelain bowl, mix 2-3 g of boric acid, 5 ml of sulphuric acid and 30 ml of methanol. Put the bowl on an asbestos-plated net. Light the mixture; a green flame is observed against a white screen.

Variant 2. In a round-bottomed flask, put 5-10 g of boric acid, 50-100 ml of alcohol, and 5-10 ml of sulphuric acid. Close the flask with a stopper through which a glass

tube with a diameter of 1 cm and a drawn-out upper end passes. Heat the mixture in the flask to boiling. Light the ether vapours of boric acid at the edge of the tube; a green flame is observed against a white screen (Fig. II-7).

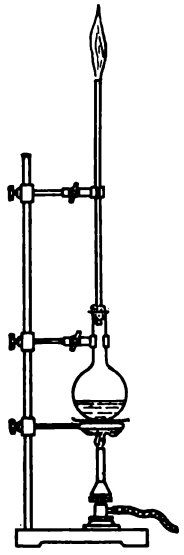


Fig. II-7. Instrument for showing how methyl borate burns

Sublimation

On heating, many volatile compounds are capable of sublimation, condensing on the cold walls of a test tube in the form of characteristic deposits. The following are easily sublimable: sulphur, selenium, iodine, chlorides of mercury (II), antimony (III) and (V), bismuth (III) and zinc, sulphides and oxides of arsenic (III) and (V), mercuric iodide and ammonium salts. On heating without aeration, organic compounds undergo dry distillation with the formation of tarry substances.

Experiment 17. Sublimation of Salts and Dry Distillation of Organic Compounds

Reagents

Ammonium chloride.
Tartaric acid.
Mercuric iodide.

Procedure. In heat-resistant test tubes (having a length of 40 cm and a diameter of 3 cm), put 1-2 g of dry ammonium chloride (the first tube), the same quantity of tartaric acid (the second one), and mercury iodide (the third one). Put the test tubes in a stand. At the lecture, heat the end of every test tube, having at first wrapped the upper part of the test tubes with filter paper which is wetted with water. Deposits appear on the walls of the test tubes: there is a white deposit in the test tube with ammonium chloride, a red deposit in the test tube with mercury iodide, and a brown tarry deposit in the test tube with tartaric acid.

Note. Sublimates may be obtained beforehand and demonstrated at the lecture in large sealed tubes with labels.

Spot Tests

The utilization of spot tests on filter paper makes it possible to increase the sensitivity of a reaction and to separate the ion mixture [16]. The spot test is based on the employment of the capillary properties of porous bodies (paper, fibre). The different sorbing ability and also the different capillary activity of ions and the different diffusion rate cause the local distribution of ions, owing to which substances accumulate and separate on paper in the form of concentric zones. Paper in an aqueous solution is usually charged negatively. Therefore, the adsorption and diffusion of colloidal particles, which carry an electric charge, are also of great importance to separation.

Ordinary filter paper is not suitable for demonstration, since it is thin and inadequately loose; for an experiment, special chromatographic paper must be used.

Spot tests are performed in the following way: by a glass tube whose end is drawn out into a capillary tube (the end must be perfectly even), a reagent is deposited on a strip of chromatographic paper, tightly pressing the capillary tube to the paper surface. In this case, the liquid must be absorbed by paper, but it should not run on the paper. Similarly, a drop of the solution being studied is deposited in the centre of the spot produced.

The advantages of such a method are especially clear when slightly soluble products are formed as a result of

Table II-6

COMPARISON OF THE SENSITIVITY OF DETECTING CATIONS BY THE TEST-TUBE AND SPOT TESTS

Cation	Reagent	Limit of detection, ppm	
		test-tube reaction	spot test on paper
Ni^{2+}	Dimethylglyoxime	3	0.3
Al^{3+}	Alizarin S	100	3
Fe^{3+}	Potassium ferrocyanide	1	0.7
Bi^{3+}	Cinchonine with potassium iodide	17	2

interaction between a reagent and a substance being analyzed. The precipitates slowly move, clogging up the paper capillaries, i.e., precipitate concentration occurs, thus increasing the sensitivity of a reaction.

Table II-6 gives the sensitivity of detecting cations by test-tube and spot methods.

Experiment 18. Detection of the Ferric Ion by Potassium Ferrocyanide

When ferric and ferrocyanide ions react, a blue precipitate known as Prussian blue is formed. The ferrous ion with the ferricyanide ion form a slightly soluble compound known as Turnbull's blue. It is very likely that these two substances are completely identical and have the formula [8] $MFe[Fe(CN)_6]$, where M is Na^+, K^+, $-\log K_{sp} = 40.5$ (25° C, $\mu \neq 0$). In comparing the oxidation-reduction potentials

$$\left(E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77 \text{ V} > E^\circ_{[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}} = 0.36 \text{ V}\right)$$

a reduction of the ferric ion by the ferrocyanide ion may be assumed. In the presence of the cyanide ion, the system $Fe^{3+} + \bar{e} \rightleftarrows Fe^{2+}$ becomes the system $[Fe(CN)_6]^{3-} + \bar{e} \rightleftarrows \rightleftarrows [Fe(CN)_6]^{4-}$, and the value of the standard potential of the latter system may be estimated by the stability constants of the cyanide complexes

$$E^\circ_{[Fe(CN)_6]^{3-}/[Fe(CN_6)]^{4-}} = 0.77 + \frac{RT}{F} \ln \frac{\beta'_6}{\beta_6}$$

$[Fe(CN)_6]^{3-}$ $\log \beta_6 = 31$

$[Fe(CN)_6]^{4-}$ $\log \beta'_6 = 24$ (25° C, $\mu \to 0$)

Reagents

Ferric chloride, 0.1 per cent solution in 0.1 *N* hydrochloric acid solution.

Potassium ferrocyanide, 10 per cent solution.

Procedure. On the demonstration table, put a beaker with 5-6 capillary tubes and a beaker with strips of filter paper (5 cm × 12 cm). At the lecture, deposit a potassium ferrocyanide solution on a strip of filter paper by a capil-

lary tube. In this case, a yellow round spot with a diameter of about 2 cm should be produced. Then, deposit a drop of an iron chloride solution in the centre of the spot by another capillary tube; a blue spot appears.

Experiment 19. Separation and Simultaneous Detection of Ferric, Nickelous and Cupric Ions

Reagents

Ferric, cupric and nickelous chlorides, 0.1 per cent solutions in 0.01 *N* hydrochloric acid solution.

Ammonia, 25 per cent solution.

Potassium ferrocyanide, 10 per cent solution, acidified by hydrochloric acid.

Dimethylglyoxime, 1 per cent ethanol solution.

Procedure. On a strip of filter paper, deposit an ammonia solution (a spot with a diameter of 2 cm), and in the centre of the spot, deposit a mixture of salt solutions; in this case, a brown spot of ferric hydroxide is formed in the centre, and a blue ring of copper ammoniate and nickel ammoniate is formed along the periphery. Then, put a drop of a potassium ferrocyanide solution on the spot of ferric hydroxide; in this case, a blue spot appears, proving the presence of iron (III). Take another capillary tube filled with a dimethylglyoxime solution and pass it along the periphery from the opposite sides of the blue spot; in this case, pink strips of nickel dimethylglyoximate are formed. Then, pass the capillary tube with a potassium ferrocyanide solution in the direction that is perpendicular to these strips; in this case, brown-violet strips of copper ferrocyanide are formed (Fig. II-8).

Note. The experiment may be carried out beforehand, and the paper chromatogram may be demonstrated with the help of an epidiascope at the lecture.

Experiment 20. Separation of a Dye Mixture by the Spot Test Method

In depositing a mixture of coloured-substance solutions, such as dyes, on filter paper, differently coloured zones are produced on the paper owing to the presence of the

particle charges of dyes and of paper and also to the difference in diffusion coefficients. The diffusion rate of methylene blue is known to be less than the diffusion rate of rhodamine dyes. Therefore, when a mixture of these dyes is deposited on paper, methylene blue remains in the centre of the spot, while the rhodamine dye moves to the periphery. When a mixture of eosin and methylene blue is

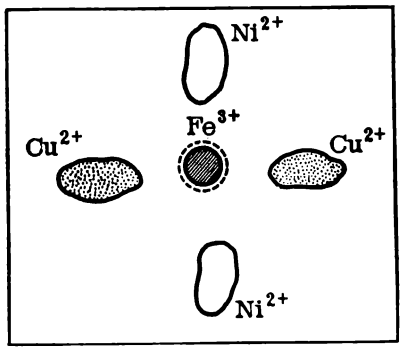


Fig. II-8. Separation and detection of the ions of iron (III), copper and nickel by the spot method

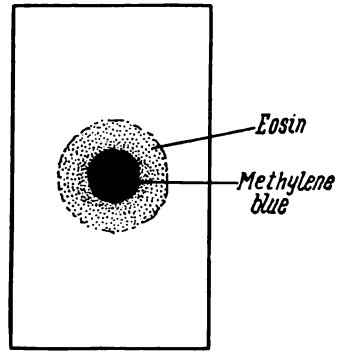


Fig. II-9. Separation of eosin and methylene blue by the spot method

deposited on paper, the latter remains in the centre of the spot, while eosin turns out to be at the periphery. This is because eosin particles have a negative charge, and methylene blue a positive one, while paper has a negative charge.

Reagents

Methylene blue, 0.01 per cent solution.

Rhodamine B, 0.01 per cent solution.

Procedure. Mix the solutions of methylene blue and rhodamine B in the ratio 1 : 1 and dilute the mixture by doubling its volume with water. At the lecture, deposit a drop of the mixture on a strip of chromatographic paper. The mixture becomes separated: a blue spot of methylene blue is observed in the centre, and a pink ring of rhodamine B, at the periphery.

Note. A similar experiment may be carried out with a mixture of eosin and methylene blue (Fig. II-9).

Analysis by Grinding Powders

Coloured reaction products are obtained when some substances are mechanically ground with reagents. Mechanical grinding helps to enlarge the surface and increase the number of contact points of particles, and to warm up reactants, thus increasing the rate of chemical reactions. Chemical interaction is promoted by crystallization water and air moisture. As a result of continuous contact with air, a hydrate film is formed on the powder surface; the film is a saturated aqueous solution of a given substance, and a reaction on the film occurs in the same way as in ordinary solutions.

The method of grinding powders is used in geological surveys; it is very convenient, because it does not require aqueous solutions of reagents [17, 18].

Experiment 21. Detection of the Nickel Ion

The afore-mentioned reaction of detecting the nickelous ion in the form of dimethylglyoximate may be performed with dry reagents. The limit of detection is 400 ppm. The ferrous ion, which also forms a red complex with dimethylglyoxime, does not interfere when the reaction is performed by the dry method, since, on grinding powders, iron dimethylglyoximate is formed only on subsequent treatment with ammonia.

Reagents
Nickelous sulphate.
Dimethylglyoxime.
Ammonium carbonate.

Procedure. In a porcelain mortar, grind 1-2 g of nickel sulphate, 4-5 g of dimethylglyoxime and some ammonium carbonate. The complex assumes a pink colour. The colour becomes more intense if the mixture is slightly wetted (for example, by breathing on it).

Experiment 22. Detection of the Cobalt Ion

Blue thiocyanate of cobalt is formed when cobalt salts are ground with ammonium thiocyanate. In aqueous solutions, the complex is unnoticed owing to the formation of

cobalt aquo ions; therefore, the blue colour disappears when the powder mixture is wetted with water.

Reagents
Cobaltous sulphate.
Ammonium thiocyanate.

Procedure. In a porcelain mortar, grind a mixture of cobalt sulphate and ammonium thiocyanate. A bright blue colouring appears; it faints when the mixture is wetted with water.

Luminescence Analysis

Many substances are capable of glowing under the action of different types of energy. All types of light emission, excluding the glow of heated bodies, are called lu-

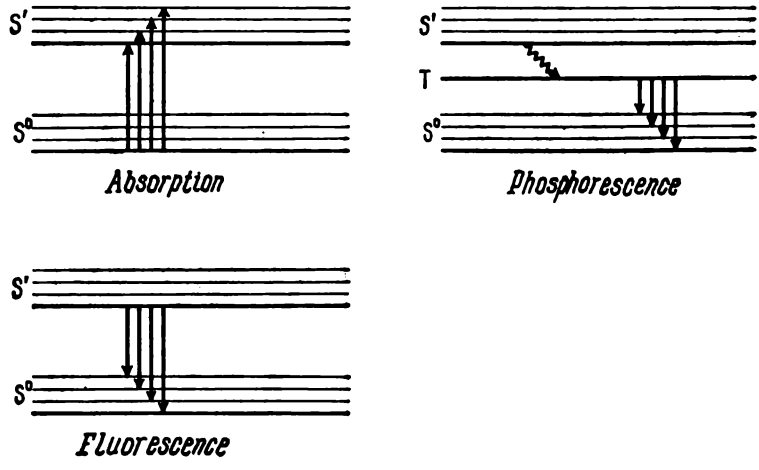


Fig II-10. Origination of the electron vibration bands of fluorescence, phosphorescence and absorption

minescence. It is not all absorbed energy that becomes luminescence energy, i.e., quanta are emitted that have lesser energy (but greater wavelength) in comparison with the absorbed quanta. The diagram in Fig. II-10 may be used to give a simple qualitative description of the possible energy states of a molecule of luminescent substances and to show that a short luminescence (fluorescence) is due to the S'-S_0 transitions of electrons, and that

a long luminescence (phosphorescence) is connected with T-S transitions, where S' and S_0 are the excited state and the normal singlet state of a molecule, respectively, and T is the excited triplet state [19].

The widest use is made of the luminescence that originates under the action of light (photoluminescence) and by a chemical reaction (chemiluminescence).

Many inorganic and organic substances are capable to luminesce. A special class of luminescent substances is represented by crystal phosphors, i.e., inorganic crystalline substances (for example, ZnS and CdS), whose lattices are deformed by the introduction of small amounts of activators: metal ions, such as Ag, Cu, Mn and U.

In analysis, luminescence is widely used for identifying substances, detecting small concentrations of substances and determining the degree of purity of a substance.

The main advantage of the luminescence method of analysis is its high sensitivity (Table II-7) [12].

Table II-7

SENSITIVITY OF SOME LUMINESCENCE REACTIONS

Ion	Reagent	Limit of detection, ppm	Ion	Reagent	Limit of detection, ppm
Be^{2+}	Morin	0.0033	Sc^{3+}	Salicylalsemi-carbazide	0.01
	Beryllon (II)	0.005			
BO_2^-	Benzoin	0.0143	Zn^{2+}	Thiooxine	0.01
Mg^{2+}	Lumomagneson	0.004	Ga^{3+}	Rhodamine B	0.002
Al^{3+}	Morin	0.0005	Zr^{4+}	Morin	0.001

For demonstrating experiments in luminescence, a quartz lamp is used; the lamp is in a metallic casing with an opening for an ultraviolet light filter, which holds back the light rays of the visible spectrum (see Fig. I-4). The lamp is switched on 5-10 minutes before the demonstration. At the same time, the windows of the auditorium are curtained.

The listeners should be shown a compound first in an ordinary light, and then in an ultraviolet light, turning the specimen so that it would be seen by all.

Experiment 23. Detection of Organic Compounds

Liminescence is especially characteristic of complex organic molecules that have a rigid structure (polycyclic aromatic or heterocyclic compounds). The excitation energy of electrons in a molecule depends on the nature of the interatomic bond. When a molecule has conjugated π-bonds, whereby the π-electrons are displaced the easier the longer the conjugation chain is, excitation energy decreases and the luminescence spectrum shifts towards long wavelengths (into the visible spectrum). For organic molecules with a non-rigid structure, molecular coplanarity is a necessary condition for luminescence.

An example of luminescent organic substances is fluorescein (λ_{max} = 520 nm), acridine (λ_{max} = 478 nm in an acid medium and λ_{max} = 425 nm in an alkaline medium), rhodamine B (λ_{max} = 560 nm) and rhodamine 6 G (λ_{max} = 580 nm).

Reagents

Rhodamine B, *rhodamine* 6 G, *acridine and fluorescein*, 0.1 per cent solutions.

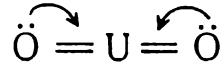
Procedure. Prepare a luminescent lamp with a light filter. At the lecture, darken the auditorium and demonstrate the luminescence of the prepared solutions, placing the bottles in the path of ultraviolet radiation. A red luminescence of rhodamine B, an orange luminescence of rhodamine 6 G, a blue luminescence of acridine (in an acid medium) and a green luminescence of fluorescein are observed under the action of ultraviolet light. Draw the listeners' attention to the absence of a luminescence when the solutions are not exposed to ultraviolet light. The sensitivity of detection of such substances is very great; at the lecture, the fluorescein solution (or any other solution) may be diluted by several fold in a vessel prepared beforehand. A luminescence is likewise observed when the diluted solution is put into the light flux.

Experiment 24. Detection of Uranic Salts

Among inorganic compounds, the salts of uranyl and of some heavy metals and lanthanoids luminesce due to

the specificity of their atomic structure (the presence of *d*- and *f*-electrons).

In a uranyl ion, the combination of d- and f-orbitals leads to the formation of single σ- and double π-bonds [8]



The luminescence spectrum is ascribed to the electron transition (such as π^*-π) in a uranyl ion on which the vibrations of the O—U—O group are superimposed. The intensity of luminescence of uranyl salts depends on the nature and concentration of anions and on the solvent. The luminescence spectra of uranyl salts consist of a series of bands in the 470-630 nm wavelength range. Among them, the most intensive bands are those in the 470-530 nm range (a greenish luminescence).

All uranyl-containing minerals luminesce when exposed to ultraviolet light. This property is used in geological survey for detecting uranium. The luminescence of the pearl of uranium with sodium fluoride is especially widely used for detecting uranium traces in natural waters.

Reagents

Zinc uranyl acetate.

Uraniferous mineral.

Procedure. Put uraniferous mineral in the path of ultraviolet light so that the illuminated surface would be seen by the audience. A bright green luminescence of the mineral is observed. If uranium minerals are unavailable, the luminescence of the precipitate of sodium zinc uranyl acetate or other uranium compounds may be demonstrated.

Experiment 25. Detection of the Aluminium Ion by Morin

As a result of complex formation between the metal ion and an organic reagent, the conjugation chain is elongated and the distribution of the electron density in the reagent molecule is changed. This leads to a decrease in

the molecular excitation energy and a change in the luminescence spectrum.

Morin in weak acid solutions forms, together with several ions, metal chelates in the ratio Me: morin 1 : 1 or 1 : 2; these compounds have an emerald green luminescence. Morin itself practically does not luminesce in 50 per cent ethanol at pH-3. The limit of detection for aluminium by the spot method is 10^{-4} ppm.

Reagents

Aluminium trichloride, solution corresponding to the aluminium concentration of 1 μg/ml.

Morin, 0.1 per cent ethanol solution.

Procedure. On two strips of chromatographic paper, deposit a morin solution (spots with a diameter of 2 cm) with a capillary tube. On one of the strips, deposit a drop of aluminium chloride solution in the centre of a spot. Demonstrate both strips with the same yellow spots to the audience in an ordinary light. Then, in the dark, put the strips of paper in the path of ultraviolet rays. A bright green luminescence is observed on a strip with aluminium salt.

Experiment 26. Detection of the Lithium Ion by 8-Hydroxyquinoline

Lithium hydroxyquinolinate brightly glows (a blue glow) under the action of ultraviolet rays. Alkali metals do not interfere with the determination of lithium.

Reagents

Lithium nitrate, 0.1 per cent solution.

8-hydroxyquinoline, 1 per cent ethanol solution.

Ammonia, 25 per cent solution.

Procedure. On a strip of paper, deposit a drop of lithium chloride solution (the diameter of the spot is 2 cm). With another capillary tube, deposit a drop of 8-hydroxyquinoline solution in the centre of the spot. Hold the spot over the bottle with an ammonia solution. Show the scarcely visible yellowish spot to the audience. Then, in the dark,

place the strip of paper in the path of ultraviolet rays. A bright blue luminescence is observed.

Note. There are some more reactions based on luminescence, such as reactions of lead or cadmium ions with pyridine, and potassium iodide, antimony and thallium ions with rhodamine B, and zirconyl ions with 3-hydroxyflavone [20].

Chromatograms may be prepared beforehand, and the luminescence may be demonstrated at the lecture, putting them in the path of ultraviolet rays.

Experiment 27. Luminescence of Crystal Phosphors

The power of some inorganic crystals to fluoresce when foreign elements, i.e., activators, are put into their lattice may be used in analysis for determining microquantities of activator ions (Table II-8) [12, 21].

Table II-8

SENSITIVITY OF DETECTING ELEMENTS (ACTIVATORS) BY THE FLUORESCENCE OF CRYSTAL PHOSPHORS

Activator	Base	Minimum which can be detected, μg	Activator	Base	Minimum which can be detected, μg
Sn	KI	$2 \cdot 10^{-4}$	Hg	CaO	$2 \cdot 10^{-2}$
Sn	CaO	$1 \cdot 10^{-4}$	Tl	KI	$1 \cdot 10^{-3}$
Sb	$K_4[Fe(CN)_6]$	$1 \cdot 10^{-3}$	Tl	CaO	$2 \cdot 10^{-2}$
Sm	CaF_2	$1 \cdot 10^{-2}$	Pb	CaO	$1 \cdot 10^{-3}$
Eu	NaCl	$1 \cdot 10^{-3}$			

The methods of preparing crystal phosphors are complicated (owing to the absence of sufficiently pure initial products). Crystal phosphors may be prepared by co-crystallizing a base and an activator or by obtaining the pearls of borax or of phosphates in the presence of activators [20]. The compositions of some crystal phosphors whose activator is 10^{-4}% Cu are given below:

ZnS, %		CdS, %	*Luminescence*
100	—	—	Green
95	—	5	Green
90	—	10	Yellow-green
85	—	15	Yellow-greenish
80	—	20	Yellow
70	—	30	Dark yellow
60	—	40	Orange
50	—	50	Red

Procedure. Put crystal phosphor powders beforehand in test tubes with a diameter of 1 cm and a height of 5 cm, and fasten them to a black screen with wire. Put a label under each test tube. At the lecture, demonstrate the luminescence of crystal phosphors in ultraviolet light. Switch off the luminescence lamp and show the after luminescence.

Experiment 28. Detection of the Tin Ion by the Crystal Phosphor Luminescence

The detection of the tin (II) ion is based on the formation of the crystal phosphor KI-Sn, which has a yellow luminescence under the action of ultraviolet rays. When the spot method is used, 0.02 μg can be detected [21].

Reagents

Tin dichloride, 0.01 per cent solution in 1 *M* hydrochloric acid solution.

Potassium iodide, 10 per cent solution.

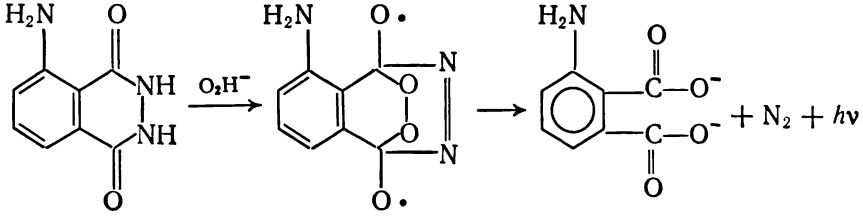
Procedure. On a strip of filter paper, deposit a drop of tin chloride solution (the diameter of the spot is 3 mm) with a capillary tube. Then, in the centre of the spot, put a potassium iodide solution with a capillary tube so that it would cover the first drop. Dry the drop on the paper a little over a burner flame and place it in the path of ultraviolet rays. A yellow luminescence is observed.

When heated too much, potassium iodide begins to decompose, and iodine that has been formed adsorbs ultraviolet rays and weakens luminescence.

Note. Similar crystal phosphors form mercuric and thallous ions.

Experiment 29. Detection of the Copper Ion by a Chemiluminescence Reaction with Luminol and Hydrogen Peroxide

Chemiluminescence is usually observed when organic compounds are oxidized by hydrogen peroxide or oxygen. For analytical chemistry, catalytic reactions are the most interesting, since the catalytic effect is the basis on which the sensitive methods of detecting elements (copper, iron, cobalt, etc.) have been worked out [22]. For example, the catalyst in the oxidation of luminol by hydrogen peroxide is copper (II), which promotes the formation of radicals. Light is emitted when radicals are recombined. The minimum which can be detected is 0.0001 μg of Cu. The reaction mechanism is very complicated and has not been completely clarified. The following pattern is the most probable one: luminol is oxidized by hydrogen peroxide in an alkaline medium according to the free-radical mechanism up to a peroxide biradical; when this biradical decomposes, a light quantum is emitted and aminophthalic acid and nitrogen are formed:



$$H_2O_2 + OH^- \longrightarrow O_2H^- + H_2O$$

Reagents

Cupric sulphate, 0.01 per cent solution.
Luminol, 0.2 per cent solution in 0.2 *M* potassium hydroxide solution.
Hydrogen peroxide, 0.3 per cent solution.
Potassium hydroxide, 2 *M* solution.

Procedure. In a large 3-litre flask, put 50 ml of luminol solution and 50 ml of potassium hydroxide solution, and dilute to 2 litres with water. At the lecture, add 20 ml of

hydrogen peroxide solution. Switch off the light; a luminescence in the flask is not observed. Add 20 ml of copper sulphate solution and shake. An intense green luminescence appears.

Note. When the excess of hydrogen peroxide is large, there may be a luminescence without the addition of copper, and the extinction of chemiluminescence is also possible.

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CHAPTER III

Introduction to quantitative analysis

Usually, at a lecture on quantitative analysis, the main problems of gravimetric and titrimetric determinations and the principles of physicochemical and physical methods of analysis are examined, a classification of methods according to the quantity of a substance being determined is presented, and the techniques of analysis are demonstrated [1-8].

The main criteria for evaluating analytical methods are accuracy and precision of determinations, and also the sensitivity and express nature of a method [see p. 35].

Sensitivity is determined by the smallest signal which may be received when a given method is used [9]. But the useful signal must be distinguished from the background signal. In other words, the difference in the two signals determines the quantity of a substance that is present; moreover, these two signals are comparable at the level or near the limit of detection. If the standard deviation of the results of measurement of signals of a blank experiment is S_b and the mean value of this signal is $\bar{X}_b$, the minimum detectable difference between the mean value of $\bar{X}$ of the signals of the test and the mean value of the signal of the blank experiment is determined as

$$\bar{X} - \bar{X}_b = K\sqrt{2}S_b$$

where K = constant which depends on the required confidence interval;

$\bar{X}$ = sum of the signal of the substance being determined and the signal of either the blank experiment or the background.

It follows from the formula that the limit of detection is determined by the ratio of the useful signal to the

fluctuations of the signal of either a blank experiment or the background $(\bar{X} - \bar{X}_b)/S_b$. If $S_b/\bar{X}_b = \text{const}$, sensitivity is determined by the ratio of the useful signal to the signal of either a blank experiment or the background.

A table of comparison of the data of sensitivity and precision of different methods of quantitative determinations may be demonstrated [10-12].

Table

SENSITIVITY AND PRECISION OF THE METHODS OF QUANTITATIVE ANALYSIS

Method	Sensitivity	Precision, %
Gravimetric	1000 ppm	0.01
Titrimetric	10^{-2} M	0.01
	10^{-5} M	0.1
	10^{-6}-10^{-7} M (with concentration)	0.2-1.0
Polarographic	10-100 ppm	0.1-0.2
	0.1-1 ppm	2-10
	0.005 ppm	20
	0.001 ppm (with concentration)	5-10
Coulometric	10-100 ppm	0.001-0.005
Spectrophotometric	0.0005-0.1 ppm	5-10
Kinetic	0.0001-0.001 ppm	20
Emission spectrographic	0.1-100 ppm	5-10
Flame photometric	0.1-10 ppm	1-5
	0.002-0.1 ppm	5-10
Atomic absorption	0.1-10 ppm	1-5
	0.005-0.1 ppm	5-10
X-ray fluorescence	20-200 ppm	0.1
γ-Resonance (Mössbauer) spectroscopy	from 0.1% to 0.0001%, depending on the thickness of the specimen	Semi-quantitative determination
Mass spectrometric:		
spark source	0.01-0.1 ppm	5-10
vacuum fusion	100 ppm (O_2, N_2, H_2)	5
	0.7 ppm	20
Neutron activation	0.001-0.01 ppm	2-10

In determining substances, it is necessary to select methods whose sensitivity is at least 10-15 times higher than

the concentrations being measured. After determining the methods that are suitable as to sensitivity, a method of admissible precision should be selected. Among the shortcomings of many physico-chemical and physical methods is their comparatively low precision of determination for high concentrations. Classical chemical methods of gravimetry and titrimetry are characterized by simplicity and precision. Therefore, chemical methods have lost none of their importance.

The ever wider utilization of pure and superpure materials in the intensively developing industries and fields of science has given rise to analytical methods that have made it possible to increase the sensitivity and precision of determining elements by several orders.

Besides being sensitive, accurate and precise, modern chemical methods of analysis must be express, routine and automatic. In such cases, use is made of physical and physicochemical methods of analysis that make it possible to effect a rapid and automatic determination and, if necessary, the remote control of the composition of substances.

The tendencies of analytical chemistry are: the combination of two or several analytical methods into a single one (for example, chromatopolarography and extraction spectrophotometry), the utilization of computers and other cybernetic devices, and the ever wider utilization of electronic computers for rapidly processing measurement results [13]. It is expedient to demonstrate several illustrations showing the modern instruments used in analytical operations and the automation of these operations; the illustrations may be borrowed from the periodicals *Instruments and Techniques of an Experiment* (in Russian), *Journal of Chemical Education*, etc.

Modern analytical chemistry is characterized by the fact that growing attention is paid to the objects of the surrounding medium as the most important field of investigation. It is expedient to put on the demonstration table a set of minerals, ores (their quantitative composition must be indicated) and other natural specimens, and also of steels and alloys. The attention of the audience may be drawn to two minerals with the same qualitative

and different quantitative compositions. For example, asbestos and talc. The composition of asbestos is: SiO_2 44.1%, MgO 43.0%, H_2O 12.9%; the composition of talc is: SiO_2 65.6%, MgO 30.6%, H_2O 3.8%; the minerals differ from one another by their appearance.

Like at the lecture on qualitative analysis, there should be a set of ware for carrying out a quantitative analysis by different methods of macro-, micro-, semimicro- and ultramicro-analysis (see Chapter II) [14].

GRAVIMETRIC ANALYSIS

Macroanalysis. A 400-ml beaker and a rubber-tipped glass rod, a 300-ml washer, a chemical funnel with a filter, an exsicator with several crucibles, a crucible with a porous bottom, porcelain, quartz, platinum, iron and nickel crucibles, a forceps, a set of ashless filters of different size, black paper filters for white precipitates, and a glass crucible with a porous bottom that has a coloured precipitate (for example, nickel dimethylglyoximate). If possible, it would do well to show a crucible or a porcelain bowl with a dark blue glaze on the inner walls that makes it possible to examine the clear dry residues after evaporation. It is also expedient to show fluoroplastic ware (a crucible, a bowl, a funnel), at the same time mentioning that fluoroplastic articles withstand a temperature of up to 300° C. In them, various operations may be carried out with aggressive reagents: nitric and hydrochloric acids, their mixture, hydrofluoric acid, alkaline solutions.

Microanalysis. A 20-ml beaker, an instrument for microfiltration, a micro-washer, and micro-crucibles and bowls.

TITRIMETRIC ANALYSIS

Macroanalysis. Graduated flasks with ground-glass stoppers having a capacity of 1 litre and 100 ml that are filled up to the mark with a coloured fluid: a permanganate solution or a potassium bichromate solution A burette with a blue strip having a capacity of 50 ml or 25 ml in

a holder (use white background!). A device may be put on an ordinary burette that makes it possible to take the reading of the fluid level without parallax (Fig. III-1).

A burette with a fluoroplastic cock should be shown. Such a cock has a good sliding surface and does not require lubrication; the cock does not get jammed when alkaline solutions are used.

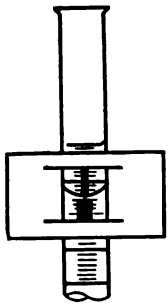

Fig. III-1. Device for reading the fluid level in a burette

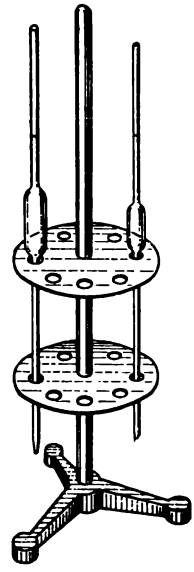

Fig. III-2. Mohr's pipettes in a holder

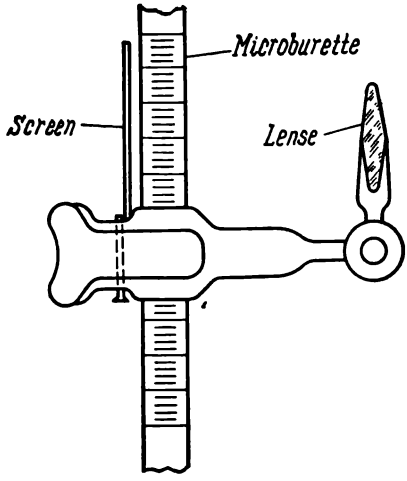

Fig. III-3. Microburette with a magnifying glass

There should also be a weight burette, a set of Mohr's pipettes with a different capacity in a special holder (Fig. III-2), conical flasks with a capacity of 300 ml and 100 ml, and a set of fixinals * of different substances (solid and liquid).

Micro- and ultramicroanalysis. A 10-ml graduated flask with a coloured solution, 1-ml and 2-ml microburettes with a magnifying glass for reading the fluid level

* Fixinal: a chemical purity solid or liquid substance with a definite number of gram-equivalents in an ampoule. — *Tr.*

(Fig. III-3), a pneumatically regulated microburette that is filled with a coloured fluid, a set of micropipettes, and

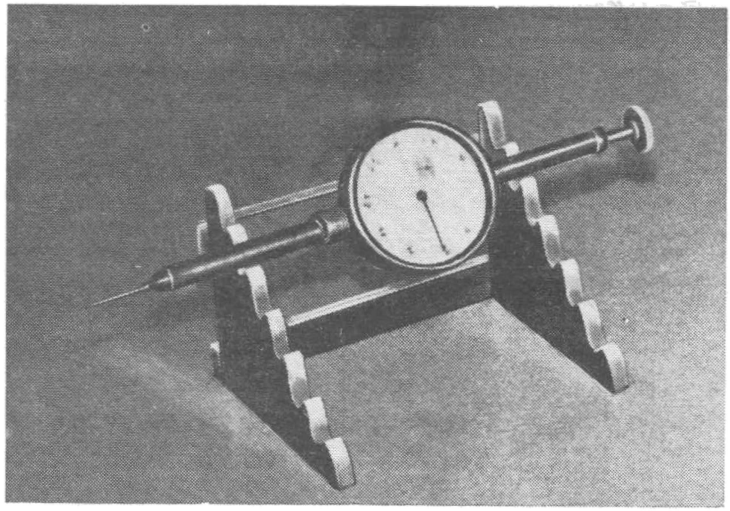

Fig. III-4. Micropipette with a dial

a micropipette with a dial (Fig. III-4) on appropriate stands.

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CHAPTER IV

Equilibrium in homogeneous systems

Most reactions used in analytical chemistry occur in solution. Therefore, in the theory of analytical chemistry, attention is mainly devoted to the chemical equilibrium of ionic reactions: the reaction direction and depth, the kinetics of reactions, and the effect of various factors on equilibrium [1].

IONS IN SOLUTION

The state of ions in solution is determined by the nature of a substance, the properties of a solvent and other factors (the presence of foreign ions, temperature, and so forth). Ions in a solution interact with the molecules of the solvent, forming solvates. The energy of interaction may be very considerable; for example, if water is the solvent, the hydration energy is 10^2-10^3 kJ/mol. Every ion in

Table IV-1

HYDRATION ENERGY OF SOME IONS, KJ/MOL

Ion	Hydration energy	Ion	Hydration energy
Li^+	520.7	NH_4^+	303.4
Na^+	405.9	F^-	505.6
K^+	322.3	Cl^-	363.3
Rb^+	300.9	Br^-	336.0
Mg^{2+}	1922.0	I^-	295.1
Ba^{2+}	1360	ClO_4^-	238.6
Sc^{3+}	2641	OH^-	460.4

an aqueous solution is surrounded by a more or less permanent shell of water molecules; moreover, cations are hydrated stronger than anions (Table IV-1) [2].

It is expedient to present an illustration of ionization, dissociation and solvation (Fig. IV-1), and also a table of values of the hydration energy of some ions.

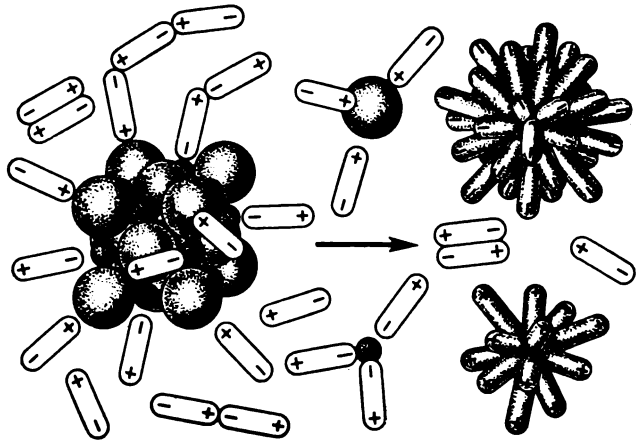

Fig. IV-1. Solvation, ionization and dissociation of molecules

Henceforth, in writing some reactions, simple ions will be presented for brevity, although it should be borne in mind that they are hydrated (solvated).

As the concentration of hydrogen ions changes, the ion state changes owing to the formation of aquo and hydroxo

Table IV-2

FORMS OF SOME IONS

Simple hydrated ion	Polymer ions	References
$[Be(H_2O)_4]^{2+}$	$\{[Be(OH)]_3(H_2O)_6\}^{3+}$	[1]
$[Al(H_2O)_6]^{3+}$	$[Al_2(OH)_2]^{4+}$, $[Al_{13}(OH)_{32}]^{7+}$	[5]
$[Zr(H_2O)_6]^{4+}$	$[Zr_4(OH)_8(H_2O)_6]^{8+}$, $[Zr_8(OH)_{22}(H_2O)_n]^{10+}$	[6]
$VO_2^+ \cdot aq$, $VO_4^{3-} \cdot aq$	$[V_{10}O_{28}]^{6-}$, $[V_2O_7]^{4-}$, $[V_4O_{12}]^{4-}$	[7]
$MoO_4^{2-} \cdot aq$	$[Mo_7O_{24}]^{6-}$, $[Mo_8O_{26}]^{4-}$	[8]

complexes, and also to polymerization. As an illustration, a diagram may be shown of the state (Fig. IV-2) of phosphate, sulphide, scandium [3], and zirconium ions [4] in

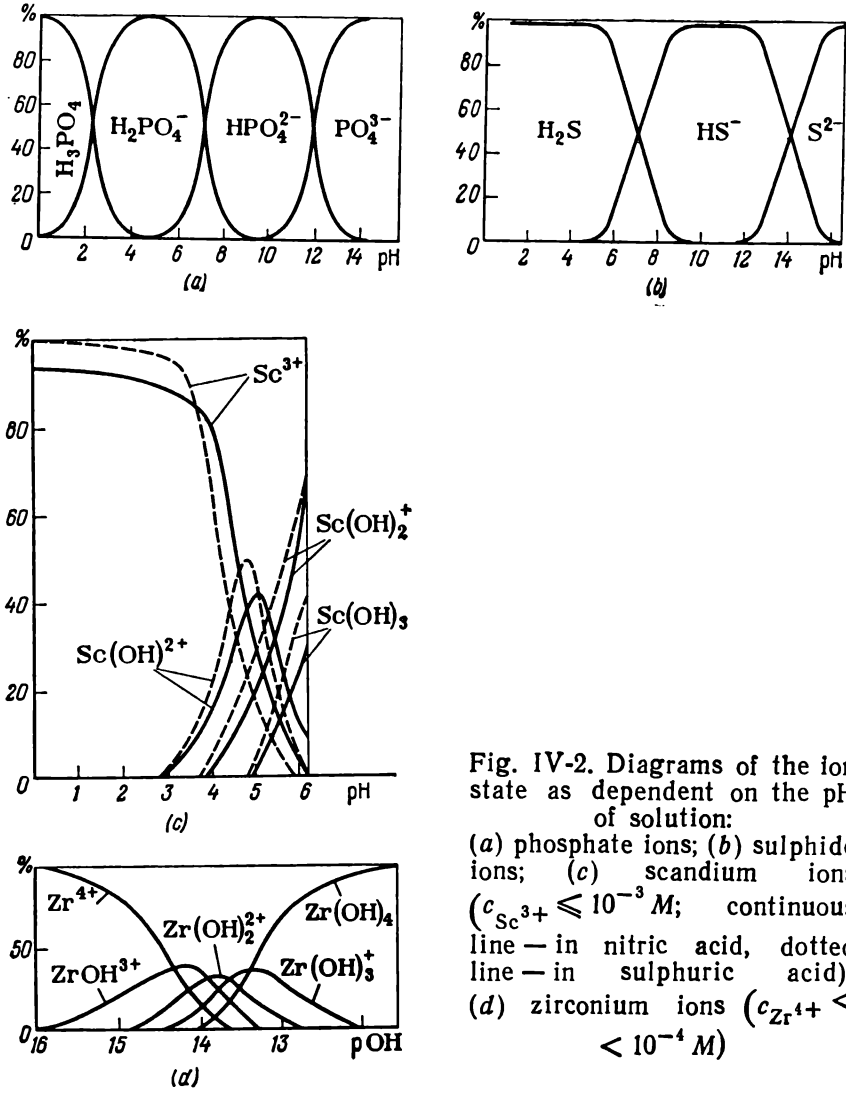

Fig. IV-2. Diagrams of the ion state as dependent on the pH of solution:
(*a*) phosphate ions; (*b*) sulphide ions; (*c*) scandium ions ($c_{Sc^{3+}} \leqslant 10^{-3}\ M$; continuous line — in nitric acid, dotted line — in sulphuric acid); (*d*) zirconium ions ($c_{Zr^{4+}} < 10^{-4}\ M$)

sufficiently dilute solutions (i.e., in the absence of polymerization), depending on the pH of the solution.

When ion concentrations are large, polymerization and formation of complex ions are observed (Table IV-2).

Experiment 30. Aquo Complexes of the Cobalt Ion

Cobaltous ions as transition metal ions form octahedral hexaquo complexes $[Co(H_2O)_6]^{2+}$ of pink colour. However, for the cobalt ion that has *d*-electrons, the stabilization energy in the field of ligands with an octahedral configuration is virtually the same as the stabilization energy in the field of ligands with a tetrahedral configuration. Therefore, the existence of a complex tetraquo ion $[Co(H_2O)_4]^{2+}$ is possible. Equilibrium between both types of ions apparently exists in solution.

The pink colour of the aqueous solutions of cobalt salts is due to the aquo complexes of the cobalt ion. The replacement of water in aquo complexes by other ligands, such as the chloride ion, and also dehydration lead to a colour change owing to the formation of a tetrahedral chloride complex:

$$[Co(H_2O)_6]^{2+} + 4Cl^- \rightleftarrows [CoCl_4]^{2-} + 6H_2O$$

Reagents

Cobaltous chloride, 10 per cent solution.
Calcium chloride or magnesium chloride, 30 per cent solution.
Hydrochloric acid, concentrated.

Procedure. *Variant 1.* In a cylinder, put 40 ml of cobalt chloride solution and 160 ml of water. At the lecture, pour the solution into two cylinders. Keep one cylinder for reference, and add to the other one an equal amount of concentrated hydrochloric acid. The colour changes from pink to dark blue.

Variant 2. In a cylinder, put 200 ml of calcium chloride (or magnesium chloride) solution. At the lecture, slowly add 20 ml of a pink solution of cobalt chloride while stirring. The solution in the cylinder becomes dark blue.

Experiment 31. Cobalt Ion Dehydration on Heating

When temperature is elevated, cobaltous aquo complexes are dehydrated possibly with the replacement of water molecules in the internal coordination sphere by chloride

(sulphate, nitrate, etc.) ions

$$[Co(H_2O)_6]Cl_2 \xrightarrow{t} [Co(H_2O)_nCl_2] + (6-n)H_2O$$

Reagent
Cobaltous chloride, 10 per cent solution.

Procedure. Pour a cobalt chloride solution into two flasks. Keep one flask for reference, and heat the other one up to 80° C. The colour changes from pink to dark blue-violet, which is characteristic of a mixture of hydrated and less hydrated cobalt ions.

Experiment 32. Inert Aquo Complex of the Chromic Ion

Unlike many transition elements, which usually form labile octahedral aquo complexes, the chromic ion is characterized by an inert (kinetically stable) aquo complex. Therefore, many chromic ion reactions proceed slowly in aqueous solution at room temperature. For example, at 25° C, there is virtually no reaction between chromic and ethylenediaminetetra-acetate (EDTA) ions, on heating, the reaction is accelerated:

$$[Cr(H_2O)_6]^{3+} + H_2Y^{2-} \rightleftarrows CrY^- + 2H^+ + 6H_2O$$

where Y = the EDTA anion.

Reagents
Chromic chloride, 1 per cent solution in 0.01 *N* hydrochloric acid solution.
EDTA, saturated solution.
Acetic acid, 2 *M* solution.

Procedure. In a 1-litre beaker of heat-resistant glass, put 200 ml of chromium chloride solution, 600 ml of water and 50 ml of acetic acid. At the lecture, pour the solution into two beakers. To each of them, add 100 ml of EDTA solution. A colour change is not observed. Heat one beaker up to 70-80° C. A crimson-violet colour characteristic of the complex of chromium with EDTA appears.

Experiment 33. State of Ions and Molecules as Dependent on the Polarity of the Solvent. Iodine Molecule Solvates

The possibility of iodine solvate formation depends on the solvent (see Experiment 7).

Reagents
Crystal iodine.
Ethanol.
Benzene.
Carbon tetrachloride.

Procedure. Take three cylinders and put in them 150 ml of ethanol (first cylinder) and the same amount of benzene (second one) and carbon tetrachloride (third one). At the lecture, add to every cylinder an equal amount of iodine crystal particles and shake (use a protective screen!). In the first cylinder, a yellow-brown solution containing solvated iodine molecules is formed; in the second one, a yellowish-violet solution containing a mixture of solvated and unsolvated iodine molecules is formed; in the third cylinder, a violet solution of unsolvated iodine molecules is formed.

Experiment 34. Chemical Activity of the Iodine Molecule Solvates

Solvated iodine molecules are more active chemically in oxidation-reduction processes than unsolvated molecules. This may be demonstrated by the interaction of the solutions of solvates of iodine molecules with mercurous chloride, continuing the preceding experiment:

$$Hg_2Cl_2 + I_2 \rightleftarrows HgI_2 + HgCl_2$$
$$HgI_2 + HgI_2 \rightleftarrows Hg[HgI_4]$$

The reaction between mercurous chloride and iodine molecules that have been solvated by ethanol proceeds considerably more rapidly than the reaction with unsolvated iodine molecules [9].

Reagent

Mercurous chloride, saturated solution.

Procedure. Add 10 ml of mercury chloride solution to the first cylinder and likewise to the third one (solutions obtained by the preceding experiment), and strongly shake them (use a protective screen!). The solution of iodine in alcohol is decolorized in 10 seconds, and the solution of iodine in carbon tetrachloride is decolorized in 3-4 minutes.

DISPLACEMENT OF CHEMICAL EQUILIBRIUM IN SOLUTIONS

Ionic equilibrium obeys the law of mass action and is quantitatively characterized by the equilibrium constant. The thermodynamic constant K^t depends only on temperature and pressure. Under real conditions, i.e., under the conditions of ultimate ionic strength and the occurrence of side (competing) reactions (protonization, complex formation, precipitation, etc.), use is made of the concentration constant K^c that depends on the ionic strength of the solution, and the conditional constant K^{con} that depends on the reaction conditions and the ionic strength [10-12]. For example:

$$A + B \rightleftarrows C + D$$

$$K^t = \frac{a_C \cdot a_D}{a_A \cdot a_B}$$

$$K^c = \frac{[C][D]}{[A][B]} = \frac{a_C \cdot a_D}{a_A \cdot a_B} \cdot \frac{f_A \cdot f_B}{f_C \cdot f_D} = K^t \frac{f_A \cdot f_B}{f_C \cdot f_D}$$

$$K^{con} = \frac{c_C \cdot c_D}{c_A \cdot c_B} = \frac{[C][D]}{[A][B]} \cdot \frac{\alpha_A \cdot \alpha_B}{\alpha_C \cdot \alpha_D} =$$

$$= \frac{a_C \cdot a_D}{a_A \cdot a_B} \cdot \frac{f_A \cdot f_B}{f_C \cdot f_D} \cdot \frac{\alpha_A \cdot \alpha_B}{\alpha_C \cdot \alpha_D}$$

Hence,

$$K^{con} = K^c \frac{\alpha_A \cdot \alpha_B}{\alpha_C \cdot \alpha_D} = K^t \frac{f_A \cdot f_B}{f_C \cdot f_D} \cdot \frac{\alpha_A \cdot \alpha_B}{\alpha_C \cdot \alpha_D}$$

where [A]-[B] ... = equilibrium ion concentration;
c_A-c_B .... = overall ion concentration;
a = ion activity;
f = activity coefficient ($f = a_A/[A]$);
α = side reaction coefficient ($\alpha = [A]/c_A$).

Effect of Ion Concentration on Equilibrium Displacement

Experiment 35. Equilibrium in Copper Chloride Solution

In an aqueous solution, cupric ions form hexaquo complexes $[Cu(H_2O)_6]^{2+}$ of a dark-blue colour. When halide ions are added, water molecules are successively replaced, forming a series of halide complexes up to $[CuCl_4]^{2-}$ of yellow-green colour. On dilution with water, equilibrium is reversely displaced, forming aquo ions. In the solid form, anhydrous copper chloride has an emerald-green colour. Crystal hydrates of copper salts, such as copper sulphate, have a blue colour owing to the coordination of water molecules by copper ions.

Variant 1

Reagent
Cupric chloride, anhydrous.

Procedure. Take three cylinders and in each of them put 50 g of dry copper chloride that has an emerald-green colour, which is characteristic of the $CuCl_2$ molecules. At the lecture, add 50 ml of water to one of the cylinders; the colour becomes green-blue, which is characteristic of mixed aquo chloride complexes of copper. To another cylinder, add 200 ml of water; the colour becomes blue, which is characteristic of the aquo-ions of copper.

Variant 2

Reagents
Cupric sulphate, 5 per cent solution.
Sodium chloride, saturated solution.

Procedure. In a cylinder, put 100 ml of copper sulphate solution. At the lecture, add an equal amount of sodium chloride solution; the blue colour changes to yellow-green.

Experiment 36. Equilibrium in Iron Thiocyanate Solution

When the ferric ion reacts with thiocyanate ions, a series of complex compounds of red colour are formed. Colour intensity grows as the number of ligands increases (see Experiment 8):

$$[Fe(H_2O)_6]^{3+} \xrightleftharpoons{NCS^-} [Fe(NCS)(H_2O)_5]^{2+} \xrightleftharpoons{NCS^-}$$
$$\log K_1 = 1.96$$
$$\rightleftharpoons [Fe(NCS)_2(H_2O)_4]^{+} \xrightleftharpoons{NCS^-} [Fe(NCS)_3(H_2O)_3] \xrightleftharpoons{NCS^-}$$
$$\log K_2 = 2.02 \qquad \log K_3 = -0.41$$
$$\rightleftharpoons [Fe(NCS)_4(H_2O)_2]^{-} \xrightleftharpoons{NCS^-} [Fe(NCS)_5(H_2O)]^{2-} \xrightleftharpoons{NCS^-}$$
$$\log K_4 = -0.14 \qquad \log K_5 = -1.57$$
$$\rightleftharpoons [Fe(NCS)_6]^{3-} \qquad [18^\circ C,\ \mu = 1.8\ (KNO_3)]$$
$$\log K_6 = -1.51$$

An increase in the concentration of the ferric ion or the thiocyanate ion leads to a change in the colour of iron thiocyanate (Fig. IV-3). A reduction in the concentration of the ferric ion by binding it into a chloride complex leads to an increase in the dissociation of iron thiocyanate and, consequently, to a fainter colour.

The logarithms of stability constants of chloride iron complexes are: $[FeCl]^{2+}$ $\log K_1 = 1.48$; $[FeCl_2]^{+}$ $\log K_2 = 0.65$; $[FeCl_3]$ $\log K_3 = -1.0$; $[FeCl_4]^{-}$ $\log K_4 = -1.92$ (25° C, $\mu \to 0$).

Reagents

Ferric chloride, 1 per cent solution in 0.1 *N* hydrochloric acid solution.

Ammonium thiocyanate, 2 per cent and 0.2 per cent solutions.

Potassium chloride, saturated solution.

Hydrochloric acid, concentrated.

Procedure. In a cylinder, put 10 ml of iron chloride solution, 10 ml of concentrated hydrochloric acid and 900 ml of water. At the lecture, add 50 ml of 0.2 per cent ammonium thiocyanate solution; a faint pink colour of iron thiocyanate appears. Pour the solution obtained into three cylinders. Keep one cylinder for reference. To ano-

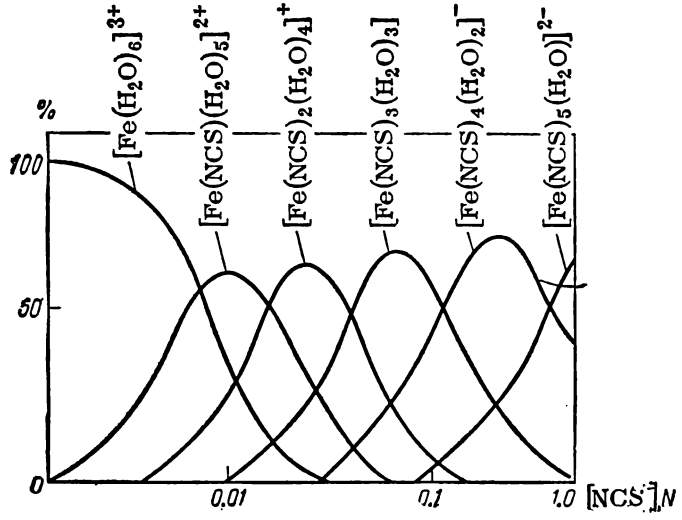

Fig. IV-3. Distribution of complex ions of iron thiocyanate

ther cylinder, add 20 ml of 2 per cent ammonium thiocyanate solution; an intensification of colour is observed. To the third cylinder, add 20 ml of potassium chloride solution; the colour fades up to light yellow, which is characteristic of the iron (III) chloride complex.

Equilibrium Displacement by the Removal of Reaction Products

Experiment 37. Reaction Between Potassium Iodide and Arsenic Acid in Frozen Aqueous Solution

The oxidation of an iodide ion by arsenic acid is a reversible reaction

$$H_3AsO_4 + 3I^- + 2H^+ \rightleftarrows HAsO_2 + I_3^- + 2H_2O$$

$$E^\circ_{H_3AsO_4/HAsO_2} = 0.559\ V,\quad E^\circ_{I_3^-/3I^-} = 0.536\ V$$

The equilibrium of the reaction may be easily displaced by various methods, for example, by freezing the solution [9].

Reagents

Potassium iodide, 0.01 *M* solution.
Arsenic acid, 0.01 *M* solution.
Perchloric acid, 0.01 *N* solution.
Carbon dioxide, solid.
Acetone.

Procedure. The solutions of arsenic and perchloric asids are preheated to boiling in order to remove carbon dioxide. After cooling, pour 20 ml of arsenic acid solution, and the same amount of perchloric acid solution and potassium iodide solution into a beaker. Pour the mixture into a test tube and lower it into a Dewar flask with a cooling mixture (a mixture of acetone with solid carbon dioxide). In two minutes, ice is formed in the test tube and the solution becomes yellow (iodine formation). Take out the test tube from the Dewar flask, lower it into a beaker with warm water and observe the decolorization of the solution against a white screen.

Effect of Organic Solvents on Equilibrium

Experiment 38. Cobalt Thiocyanate Dissociation

Depending on the conditions, cobaltous ions form with thiocyanate ions a series of complexes whose spectra of light absorption are characterized by the presence of different absorption bands [13]

$$[Co(H_2O)_6]^{2+} \overset{NCS^-}{\rightleftharpoons} [Co(NCS)(H_2O)_5]^{+} \overset{NCS^-}{\rightleftharpoons}$$

$$\log \beta_1 = 0.95 \qquad \lambda_{max} = 530 \text{ nm}$$

$$\rightleftharpoons [Co(NCS)_2(H_2O)_4] \overset{NCS^-}{\rightleftharpoons} [Co(NCS)_3(H_2O)]^{-} \overset{NCS^-}{\rightleftharpoons}$$

$$\log \beta_2 = 1.6 \qquad \lambda_{max} = 570 \text{ nm} \qquad \log \beta_3 = 1.8 \qquad \lambda_{max} = 620 \text{ nm}$$

$$\rightleftharpoons [Co(NCS)_4]^{2-}$$

$$\log \beta_4 = -0.3 \qquad \lambda_{max} = 620 \text{ nm} \qquad (20^\circ \text{ C}, \mu = 1.5)$$

The presence of the last two complex forms of cobalt thiocyanate causes the blue colour of the solution. To carry out the reaction between cobalt and thiocyanate ions, owing to the low stability of the complexes, there must be either a large excess of thiocyanate ions or organic solvents (alcohol, acetone) that suppress the dissociation of a complex and promote the dehydration of aquo ions. Depending on the percentage of acetone, $\log \beta_4$ has the following values: 4.11 (40%); 5.38 (50%); 6.59 (60%); 13.72 (100%).

Reagents

Cobaltous chloride, 1 per cent solution.
Ammonium thiocyanate, 20 per cent solution.
Acetone.
Sulphuric acid, 2 *M* solution.

Procedure. In a cylinder, put 10 ml of cobalt chloride solution, 5 ml of sulphuric acid solution and 50 ml of water. At the lecture, add 40 ml of ammonium thiocyanate solution. The solution becomes only slightly pink. Add an equal amount of acetone and stir. The solution becomes bright blue.

Effect of pH on Equilibrium

Experiment 39. Equilibrium in Potassium Chromate Solution

In an alkaline solution, the chromium (VI) ion exists in the form of a yellow tetrahedral chromate ion (λ_{max} = = 366 nm). As the pH drops, chromate ions are protonized with the formation of $HCrO_4^-$ ions and subsequent dimerization:

$$\left.\begin{array}{lll} CrO_4^{2-} + H^+ \rightleftarrows HCrO_4^- & & pK_1 = 6.5 \\ HCrO_4^- + H^+ \rightleftarrows H_2CrO_4 & & pK_2 = -0.98 \\ 2HCrO_4^- \rightleftarrows Cr_2O_7^{2-} + H_2O & & \log K = 1.6 \end{array}\right\} (25°,\ \mu \to 0)$$

$$Cr_2O_7^{2-} + H^+ \rightleftarrows HCr_2O_7^-$$

As a result of the formation of biochromate ions, the solution becomes orange (λ_{max} = 349 nm) [14]. The given pattern of a reaction is valid only for solutions containing

nitric, perchloric or dilute hydrochloric and sulphuric acids. Such complexes as $[CrO_3Cl]^-$ and $[CrO_3(SO_4)]^{2-}$ are formed in the concentrated solutions of the last two acids.

Reagents

Potassium chromate, 1 per cent solution.
Hydrochloric acid, 1 *M* solution.

Procedure. In a cylinder, put a potassium chromate solution. At the lecture, pour the solution into two cylinders. Keep one cylinder for reference. To the other cylinder, add 20 ml of hydrochloric solution; the lemon-yellow colour changes to orange (use a white screen!).

Experiment 40. Equilibrium in the Ferric Ion-Sulphosalicylic Acid System

The ferric ion forms with sulphosalicylic acid metal chelates of different colour, depending on the pH of the medium. When pH is $1.8 \div 2.5$, a violet-pink complex cation of iron monosulphosalicylate, $[FeSal]^+$, is formed. In the pH range of $4 \div 8$, a red-brown complex anion of iron disulphosalicylate, $[Fe(Sal)_2]^-$, is formed. In an alkaline medium at pH $= 8 \div 12$, a yellow anion complex of iron trisulphosalicylate, $[Fe(Sal)_3]^{3-}$, is also formed. At pH $>$ $>$ 12, iron sulphosalicylate decomposes with precipitation.

The compounds of mono- and trisulphosalicylate of iron that are being formed have an absorption maximum at $\lambda = 510$ nm and 416 nm, respectively. The stability constants are: $[FeSal]^+$ $\log K_1 = 14.64$; $[Fe(Sal)_2]^-$ $\log K_2 = 10.54$; $[Fe(Sal)_3]^{3-}$ $\log K_3 = 6.94$ (18° C, $\mu = 0.25$); the limit of detection for iron in the form $[Fe(Sal)_3]^{3-}$ is 0.04 ppm.

Reagents

Ferric chloride, 0.1 per cent solution in 0.01 *N* hydrochloric acid solution.
Sulphosalicylic acid, 10 per cent solution.
Acetic acid, 2 *M* solution.
Ammonia, 10 per cent solution.

Procedure. In a 1-litre cylinder, put 50 ml of iron chloride solution, 20 ml of acetic acid and 800 ml of water. At

the lecture, add 100 ml of sulphosalicylic acid solution and stir. A violet colour of iron monosulphosalicylate appears. Pour the solution into three cylinders. Keep one cylinder for reference. To the second cylinder, add 5 ml of ammonia solution; the violet colour changes to red. To the third cylinder, add 50 ml of ammonia solution; the violet colour changes to yellow.

Equilibrium Displacement under the Action of Light

Experiment 41. Photochemical Reduction of Thionine

Iron (II) is oxidized by thionine in the light. The reaction is reversible, and in the dark it proceeds reversely:

$$\underset{\text{violet}}{Fe^{2+} + C_{12}H_9N_3S} \overset{H^+}{\rightleftarrows} \underset{\text{colourless}}{Fe^{3+} + C_{12}H_9N_3SH}$$

In an acid medium, thionine forms a cation of a violet colour. In reducing it, colourless semithionine is formed [9].

Reagents

Ferrous sulphate, 0.4 per cent solution in 0.2 *N* sulphuric acid solution.
Thionine, 0.02 per cent solution.
Sulphuric acid, 3 *M* solution.

Procedure. Into a beaker pour 480 ml of iron sulphate solution, 10 ml of thionine solution and 10 ml of sulphuric acid. The solution has a violet colour. Illuminate the beaker with a lamp of 300-500 W; put the lamp 3-4 cm away from the solution surface. The solution almost immediately becomes colourless. Set the lamp aside and put a black cover on the beaker. After several seconds, remove the cover. The solution again assumes a violet colour.

Effect of Temperature on Equilibrium

Experiment 42. Heating the Crystal Hydrate of Sodium Acetate

In heating the crystal hydrate of sodium acetate, dehydration and interaction of an acetate ion with water occur:

$$CH_3COONa \cdot 2H_2O \rightleftarrows CH_3COOH + NaOH + H_2O$$

Equilibrium displacement may be traced by using the appropriate indicators.

Reagents

Sodium acetate, crystalline.

Phenolphthalein, 0.1 per cent ethanol solution.

Procedure. In a round-bottomed flask having a capacity of 100-200 ml, put crystalline sodium acetate and 5-6 drops of phenolphthalein solution, and stir. Stopper the flask and keep for demonstrations. At the lecture, remove the stopper and slightly heat the flask; a crimson colour appears. On cooling, the colour disappears.

Note. For the theme "Displacement of Chemical Equilibrium", use may also be made of Experiments 8, 30, 31, 32, 47, 48.

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CHAPTER V

Acid-base equilibrium

Acid-base equilibrium is a particular case of equilibrium in a homogeneous system. Nevertheless, experiments concerning this section have been separated into a special chapter, which deals with buffer solutions, the determination of hydrogen ion concentration, and salt hydrolysis. All this is important in many sections of analytical chemistry (acid-base titration, precipitation and separation, and so forth) [1-3].

The acid-base properties of a molecule or an ion are exhibited during interaction with the solvent molecules. According to Brönsted and Lowry's proton theory, acids are proton donors, and bases are proton acceptors. A solvent molecule, which is capable of accepting and likewise losing protons, may act as a proton-donor acid or a proton-acceptor base. Such amphiprotic solvents may be water, alcohols, carboxylic acids, etc.:

$$\underset{\text{acid 1}}{HA} + \underset{\text{base 2}}{S} \rightleftarrows \underset{\text{base 1}}{A^-} + \underset{\text{acid 2}}{SH^+}$$

where S = solvent;

SH^+ = lyonium ion (if S is water, H_3O^+ is an oxonium ion).

The equilibrium constant of the reaction is expressed by the equation:

$$K = \frac{[A^-][SH^+]}{[HA][S]}$$

Hence, the acid ionization constant is:

$$K_a = \frac{[A^-][SH^+]}{[HA]}$$

For the base A^-, the following equilibrium is established in the solution:

$$A^- + S \rightleftarrows HA + S^-$$

Hence, the base ionization constant is:

$$K_b = \frac{[HA]\,[S^-]}{[A^-]}$$

Multiplying the value of K_a and K_b, we obtain an expression that shows the ratio between K_a and K_b for conjugate acid-base systems and the solvent autoprotolysis constant (K_S)

$$K_a \cdot K_b = [SH^+]\,[S^-] = K_S$$

For aqueous solutions, the autoprotolysis constant is denoted by K_w; $K_w = [H_3O^+]\,[OH^-] = 10^{-14}$ (25° C).

Further, in order to simplify the writing of chemical reactions, the ion H^+ will be written instead of the oxonium ion H_3O^+.

ACID-BASE EQUILIBRIUM IN AQUEOUS SOLUTION

Buffer Solutions

The aqueous solutions of the mixture of HA acid and its conjugate base A^- are buffer solutions. On dilution and addition of small amounts of acids or alkalies, the pH of buffer solutions changes insignificantly. The buffer capacity [1] depends on the concentration of acids or bases and their salts, on the ratio of the concentrations of acids and salts, and also on the acid ionization constants. The pH value of a buffer solution is calculated by the formula:

$$pH = pK_a - \log \frac{[HA]}{[A^-]}$$

Experiment 43. Buffer Action of Acetate Buffer Solution

An acetate buffer solution, which contains equal amounts of acetic acid ($pK = 4.8$) and sodium acetate, has a pH of approximately 5. To illustrate the buffer action, it is

convenient to use the congo red indicator with the pH range of the colour change being 3.0-5.2.

Reagents
Acetic acid, 30 per cent solution.
Sodium acetate, saturated solution.
Hydrochloric acid, 0.1 *N* solution.
Sodium hydroxide, 5 per cent solution.
Congo red, 0.01 per cent solution.

Procedure. Take three cylinders and in each of them put 10 ml of acetic acid, 200 ml of water and 2 ml of congo red solution. The solutions have a dark blue colour. Add 50 ml of saturated sodium acetate solution to the first cylinder and likewise to the second one. The colour of the solution changes from dark blue to pink (the pH change is from 2.7 to 5.2) owing to the formation of a buffer mixture. To the first cylinder, add 50 ml of hydrochloric acid solution; the colour does not change. To the second cylinder, add 50 ml of sodium hydroxide solution; the colour does not change either. For comparison, add 50 ml of sodium hydroxide solution to the third cylinder, which has no buffer mixture. The dark blue colour sharply changes to pink.

Experiment 44. Buffer Action of Phosphate Buffer Solution

A buffer solution containing equal amounts of sodium hydrophosphate and potassium dihydrophosphate has a pH of approximately 7. The following equilibrium exists in the solution:

$$PO_4^{3-} \overset{H^+}{\rightleftarrows} HPO_4^{2-} \overset{H^+}{\rightleftarrows} H_2PO_4^- \overset{H^+}{\rightleftarrows} H_3PO_4$$

$$pK_3 = 12.36 \quad pK_2 = 7.22 \quad pK_1 = 2.17 \quad (25^\circ\,C,\ \mu \to 0)$$

Reagents
Sodium hydrophosphate and potassium dihydrophosphate, a mixture of equal amounts of 1 *M* solutions.
Hydrochloric acid, 0.1 *N* solution.
Sodium hydroxide, 0.1 *N* solution.

Universal indicator "PKC", 0.1 per cent solution in 80 per cent ethanol solution. It has the following colour, depending on the pH:

pH	1.0	2.0	3.0	4.0	5.0
Colour	crimson	pink-orange	orange	yellow-orange	yellow
pH	6.0	7.0	8.0	9.0	10.0
Colour	greenish-yellow	yellow-green	green	dark blue-green	greyish-blue

The composition of the "PKC" indicator: bromocresol purple, 0.006 g; bromocresol green, 0.01 g; methyl orange, 0.02 g; tropeolin 00-0.04 g; phenolphthalein, 0.04 g; thymol blue, 0.05 g; bromothymol blue, 0.1 g.

Procedure. In one cylinder, put 400 ml of water, and in another, 400 ml of phosphate buffer solution; add 5 ml of universal indicator solution to one cylinder and likewise to the other one. The solutions become greenish-yellow (the cylinder with water) and yellow-green (the cylinder with a buffer solution). Pour water into both cylinders and add 20 ml of hydrochloric acid solution to one cylinder, and 20 ml of sodium hydroxide solution to the other one. In the first cylinder, the colour sharply changes to pink, and in the second, to greyish-dark blue. Pour a buffer solution into two cylinders. The colour does not change when acid or alkali is added.

Hydrolysis

According to the Brönsted-Lowry proton theory, hydrolysis is a protolytic reaction. The acidic properties of metal ions are due to the proton yield by hydrated ions:

$$[M(H_2O)_n]^{m+} + H_2O \rightleftarrows [M(H_2O)_{n-1}(OH)]^{(m-1)+} + H_3O^+$$

For the ammonium ion, the following equilibrium is observed:

$$NH_4^+ + H_2O \rightleftarrows NH_3 + H_3O^+$$

In the solutions of salts of a weak acid and a strong base, an anion will be the base, and it accepts a proton by the reaction

$$A^- + H_2O \rightleftarrows HA + OH^-$$

Hence, classical hydrolysis constants may, for the first two reactions, be regarded as the acid ionization constant, and for the last reaction, as the base ionization constant

$$K_h = \frac{K_w}{K_b} = K_a; \quad K_h = \frac{K_w}{K_a} = K_b$$

A table of ionization (hydrolysis) constants of some aquo ions (Table V-1) [4] may be presented in the auditorium.

Table V-1

IONIZATION (HYDROLYSIS) CONSTANTS OF SOME AQUO IONS AT 25° C

Ion	pK_a, h	Ion	pK_a, h	Ion	pK_a, h
Hg_2^{2+}	5.0	Ni^{2+}	10.6	Al^{3+}	5.1
Mg^{2+}	11.4	Cu^{2+}	6.8	Sc^{3+}	5.1
Ca^{2+}	12.6	Zn^{2+}	8.8	In^{3+}	4.4
Ba^{2+}	13.2	Cd^{2+}	9.0	Bi^{3+}	1.6
Mn^{2+}	10.6	Hg^{2+}	3.7	Cr^{3+}	3.8
Fe^{2+}	9.5	Sn^{2+}	3.9	Co^{3+}	0.7
Co^{2+}	8.9	Pb^{2+}	7.8	Fe^{3+}	2.2

Experiment 45. Antimonous Salt Hydrolysis

Antimonous chloride in hydrochloric acid solutions forms the soluble complex compounds $H[SbCl_4]$ and $H_3[SbCl_6]$. On dilution with water, the salt hydrolyzes with the formation of insoluble oxo chlorides of white colour, such as SbOCl or $Sb_4O_5Cl_2$.

Reagents

Antimonous chloride, 1 per cent solution in 2 *M* hydrochloric acid solution.

Hydrochloric acid, concentrated.

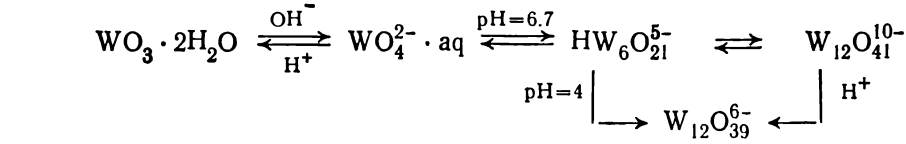
Procedure. In a cylinder, put 200 ml of antimonous chloride solution. At the lecture, add from the wash-bottle 100-150 ml of water against a black screen. A white loose precipitate of antimony oxo chloride appears.

Note. (1) A similar experiment may be carried out with bismuthous, antimonic and mercuric salts.

(2) The experiment may be continued, showing suppression of hydrolysis. For this purpose, divide the solution with the precipitate into two parts and to one part add a concentrated hydrochloric acid solution. The precipitate dissolves.

Experiment 46. Hydrolysis of Sodium Tungstate

Tungstate hydrolyzes with the formation of tungstic acids of different composition, the simplest one of which is $WO_3 \cdot 2H_2O$. When the pH decreases, the degree of tungstate polymerization increases. Apparently, the transformations in aqueous solutions may be represented by the following pattern [5]:



Reagents

Sodium tungstate or ammonium tungstate, 2 per cent solution.

Hydrochloric acid, 6 *M* solution.

Procedure. Put a sodium tungstate solution in a cylinder. At the lecture, add hydrochloric acid. The appearance of a white precipitate of tungstic acid is observed against a black screen. On boiling, $WO_3 \cdot 2H_2O$ becomes $WO_3 \cdot H_2O$ of yellow colour.

Experiment 47. Effect of Temperature on the Degree of Sodium Dihydrophosphate Hydrolysis

The degree of hydrolysis increases on heating due to the greater dissociation of water; this causes a change in the pH of the solution. This effect may be observed with the aid of a suitable indicator. Hence, in an aqueous solution of sodium dihydrophosphate, the pH is approximately 4.8 due to hydrolysis.

$$H_2PO_4^- + H_2O \rightleftarrows H_3PO_4 + OH^-$$

On heating, the pH increases and becomes 6.2 at 90° C. In this case, use may be made of cochineal as an indi-

cator, which changes the colour from yellow to lilac in the pH range of 4.8-6.2. Instead of cochineal, which is a natural substance not easily available, use may be made of its dyeing part, i.e., carminic acid.

Reagents

Sodium dihydrophosphate, 0.1 *M* solution.
Cochineal or *carminic acid*, 0.1 per cent solution.

Procedure. In a 1-litre beaker, put a sodium dihydrophosphate solution (pH $\approx$ 4.8) and add a solution of cochineal or carminic acid. The solution becomes yellow. Heat the solution almost to boiling. The indicator becomes lilac.

Note. See also Experiment 42.

Experiment 48. Effect of Temperature on the Degree of Ferric Chloride Hydrolysis

The initial stage of ferric salt hydrolysis is described by the following equations [5]:

$$[Fe(H_2O)_6]^{3+} \rightleftarrows [Fe(OH)(H_2O)_5]^{2+} + H^+ \qquad (pK_1 = 3.05)$$

$$[Fe(OH)(H_2O)_5]^{2+} \rightleftarrows [Fe(OH)_2(H_2O)_4]^{+} + H^+ \qquad (pK_2 = 3.26)$$

$$2\,[Fe(H_2O)_6]^{3+} \rightleftarrows [Fe(OH)_2(H_2O)_4 \cdot Fe(H_2O)_4]^{4+} + 2H^+ + 2H_2O \qquad (pK_3 = 2.91)$$

On heating, compounds of greater polymerization and ultimately gels are formed; these gels precipitate in the form of a red-brown mass ($-\log K_{sp} = 39.43$). On standing, a freshly-precipitated modification changes to a less soluble form

$$Fe_2O_{3\alpha} \cdot aq \quad \text{with} - \log K_{sp} = 42.7 \quad (25^\circ C,\ \mu \to 0)$$

Reagent

Ferric chloride, 1 per cent solution to which 1 ml of 0.1 *N* hydrochloric acid solution is added per 100 ml of solution.

Procedure. Put 800 ml of iron chloride solution in a heat-resistant 1-litre beaker. At the lecture, pour a part of

the solution into another beaker and keep it for reference. Heat the solution in the first beaker. The solution grows brown due to the formation of ferric aquo hydroxocomplexes in a colloidal state. If there is enough time at the lecture, it is possible by long boiling (20-30 min) to coagulate the colloid and obtain precipitate in the form of red-brown flakes. Observe the colour change against a white screen.

Experiment 49. Effect of the Iron Ion Charge on the Degree of Hydrolysis

In aqueous solutions, ferric and ferrous ions are in the form of the hexaquo complexes $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{2+}$. The water molecules bound to the metal ion tend to yield one proton or more:

$$[M(H_2O)_6]^{m+} + nH_2O \rightleftarrows [M(H_2O)_{6-n}(OH)_n]^{(m-n)+} + nH_3O^+$$

Usually, the tendency towards hydrolysis grows as the metal ion charge increases. Therefore, the formation and precipitation of polynuclear aquo hydroxocomplexes of the ferric ion are observed already at pH $\geqslant$ 3, and of the ferrous ion, at pH $\geqslant$ 7.5 ($-\log K_{sp Fe_2O_3 \cdot xH_2O} = 39.43$; $-\log K_{sp Fe(OH)_2} = 15.1$).

Reagents
Mohr's salt, 0.01 *M* solution.
Ammonium chloride, 2 *M* solution.
Ammonium persulphate, 10 per cent solution.
Ammonia, 1 *M* solution.

Procedure. Put 200 ml of ammonium chloride solution and 4 ml of ammonia solution in a cylinder. At the lecture, add 50 ml of Mohr's salt solution and rapidly stir. A ferrous hydroxide precipitate is not formed. In the course of time, Fe^{2+} is oxidized by atmospheric oxygen to Fe^{3+}, and a brown film of ferric hydroxide appears on the solution

surface. To accelerate oxidation, 20 ml of ammonium persulphate solution may be added. Perform the experiment against a white screen.

Experiment 50. Suppression of Ferric Salt Hydrolysis by Complex Formation

To prevent ferric salt hydrolysis, use may be made of the power of ferric ions to form stable complexes. The ferric ion forms stable complexes with oxalic, tartaric and citric acids and with ethylenediaminetetraacetic acid. Many complexes are formed by iron (III) with such halide ions as $[FeX_4]^-$, the most stable ones of which are fluoride complexes. The stability constants of some iron (III) complexes at 25° C are given below:

Ligand	$\log \beta_n$
Oxalate ion . . .	20.46 ($n = 3$, $\mu = 0.5$)
Tartrate ion . . .	11.86 ($n = 2$)
Citrate ion . . .	11.56 ($n = 1$, $\mu = 0.1$)
Fluoride ion . . .	11.86 ($n = 3$, $\mu = 0.5$)
Chloride ion . . .	−0.79 ($n = 4$, $\mu \to 0$)
EDTA ion	25.1 ($n = 1$, $\mu = 0.1$)

Reagents

Ferric chloride, 1 per cent solution in 0.1 *N* hydrochloric acid solution.
Tartaric acid, 10 per cent solution.
Ammonia, 25 per cent solution.
Hydrochloric acid, 6 *M* solution.

Procedure. In a cylinder, put 30 ml of iron chloride solution, dilute to 350 ml with water and add 50 ml of 6 *M* hydrochloric acid solution. At the lecture, draw the listeners' attention to the green-yellow colour of the solution due to the formation of the $[FeCl_4]^-$ ions. Pour the solution into two cylinders. To one of the cylinders, add 50 ml of ammonia solution; a red-brown flaky precipitate of iron hydroxide is formed. To the other cylinder, add 50 ml of tartaric acid solution and 50 ml of ammonia solution; a precipitate is not formed.

Note. Instead of tartaric acid, use may be made of oxalic, citric or ethylenediaminetetraacetic acid, or ammonium fluoride.

ACID-BASE EQUILIBRIUM IN NON-AQUEOUS SOLVENTS

The dependence of the acid ionization and base ionization constants on the autoprotolysis constant of a solvent explains the levelling and differentiating action of solvents [6].

It is expedient to show the audience a table of autoprotolysis constants of some solvents [7] (Table V-2).

Table V-2

VALUES OF pK_S OF VARIOUS SOLVENTS

Solvent	Lyonium ion	Lyate ion	pK_S
Sulphuric acid	$H_3SO_4^+$	HSO_4^-	3.0
Formic acid	$HCOOH_2^+$	$HCOO^-$	6.2
Acetic acid	$CH_3COOH_2^+$	CH_3COO^-	12.6
Water	H_3O^+	OH^-	14
Methanol	$CH_3OH_2^+$	CH_3O^-	16.7
Ethanol	$C_2H_5OH_2^+$	$C_2H_5O^-$	19.1
Ammonia (at −33.4°)	NH_4^+	NH_2^-	22

The relative strength of acids and bases in different solvents is influenced by dielectric constant, solvation, acid or base properties of the solvent, and the molecular structure of the latter. In solvents whose autoprotolysis constants are lower than the water autoprotolysis constant, the strength of acids decreases (or it is not manifested at all), while the strength of bases grows; the basicity of strong bases levels out, and that of weak bases differentiates. The values of pK_a (25° C) in alcohol and water are given below [1]:

	in ethanol	in water
Formic acid	9.15	3.75
Acetic acid	10.32	4.76
Cyanoacetic acid	7.49	2.47
Benzoic acid	10.25	4.20
Salicylic acid	8.68	3.00
Anilinium ion	5.70	4.63
o-Toluidinium ion	5.55	4.46
m-Toluidinium ion	5.78	4.77
p-Toluidinium ion	6.24	5.10
N-Methylanilinium ion	4.86	4.84

Experiment 51. Differentiating Effect of Solvents on Acid Strength

It is convenient to show the differentiating effect of solvents by taking the example of a change in the pK_a of picric and salicylic acids in water and acetone: in water, the pK_a of picric acid is 0.8, and in acetone, 3.2; the pK_a of salicylic acid in water and acetone is 3.0 and 9.5, respectively.

Reagents

Salicylic acid.
Picric acid.
Acetone.
Universal indicator "PKC", saturated acetone solution (see p. 99).

Procedure. Take two cylinders and in each of them put 200 ml of water; take another two cylinders and in each of them put 200 ml of acetone. At the lecture, add 0.3 g of salicylic acid to one of the cylinders with water, and 0.3 g of picric acid to the other cylinder with water; then, add 10 ml of indicator solution to each of the two cylinders. Stir the contents of the cylinders until the additives are dissolved. Note that the aqueous solution of salicylic acid has an orange colour, and the aqueous solution of picric acid has a pink-orange colour. Then, add 0.3 g of picric acid to one of the cylinders with acetone, 0.3 g of salicylic acid to the other cylinder with acetone, and 10 ml of in-

dicator solution to each of the two cylinders. Stir. Note that in the cylinder with picric acid the colour is orange, and the acetone solution with salicylic acid has a greenish-yellow colour.

ACID-BASE INDICATORS

The pH indicators, being acid-base systems, are used to determine hydrogen ion concentration in different solutions, and also the end of reactions if hydrogen ions participate in them. An index of a change in hydrogen ion concentration may be both the origination or change of colour (colour indicators [8, 9, 10]), and the appearance or disappearance of luminescence (fluorescent and chemiluminescent indicators [10-12]).

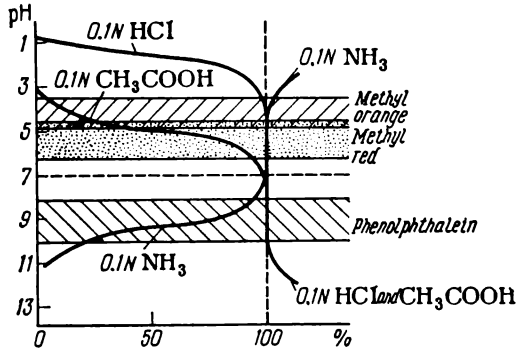
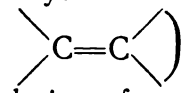


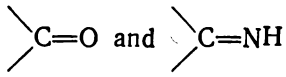
Fig. V-1. Titration curves of strong and weak acids and bases

At a lecture on acid-base indicators, the demonstration table should have a set of indicator paper, coloured scales, and a comparator with a set of light filters. A pH-meter with a glass electrode may also be put on the table. It is expedient to show the titration curves of acids, bases and salts with plotted colour transitions of indicators (Fig. V-1). Tables with pH colour transitions of colour indicators and fluorescent indicators should also be presented (see p. 109).

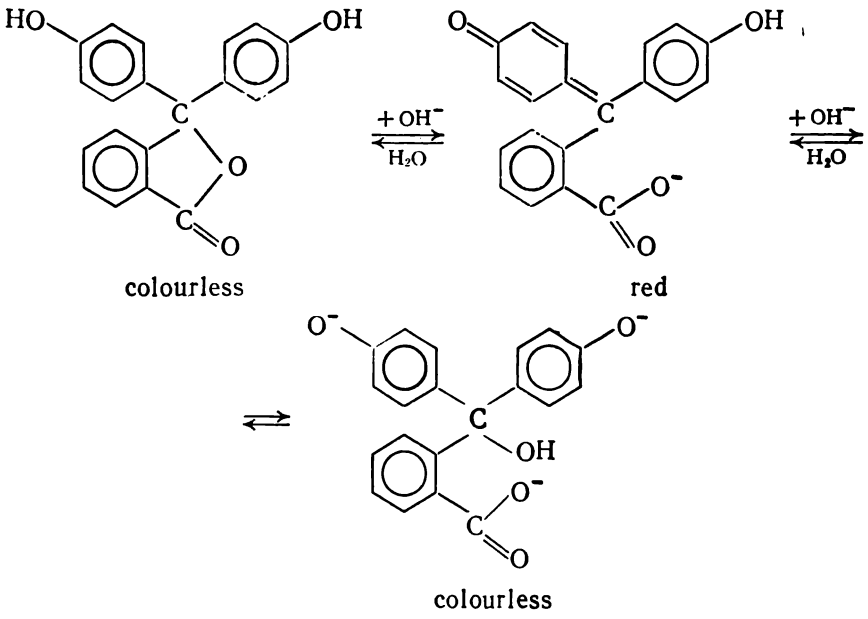
Colour Indicators

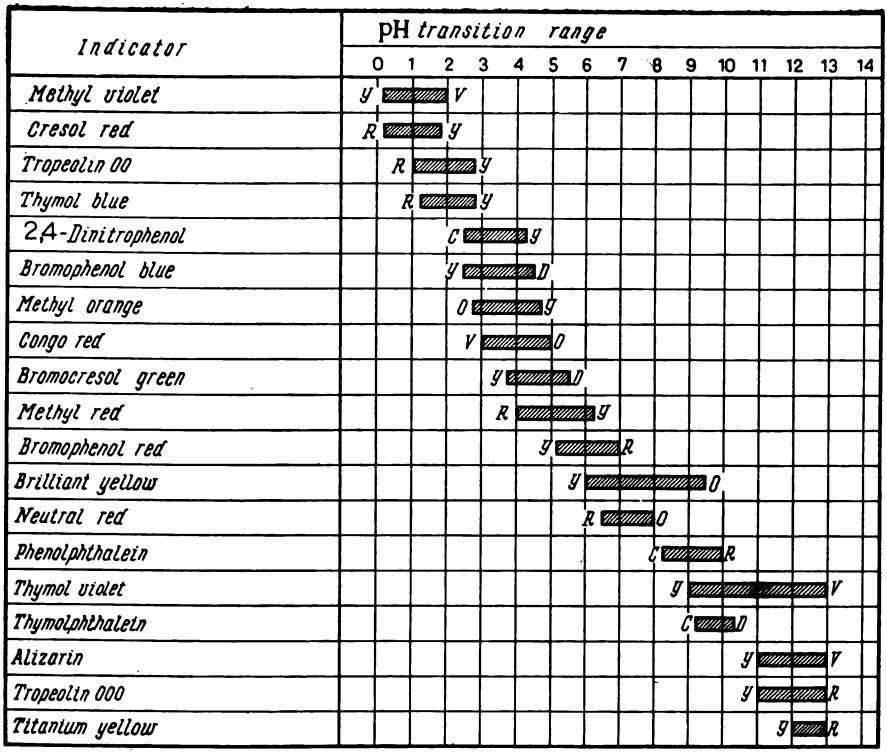
As it follows from the main principles of the theory of chromaticity of organic compounds, including colour indicators, the colour of a compound is connected with the

presence in it of unsaturated bonds [9]. The base of a chromophoric system is a chain of conjugate bonds (—N=N—;  or some isolated, competing or overlapping chains of conjugate bonds, and also electron-donor and electron-acceptor substituents that are attached to the conjugate system, and finally all the structural elements influencing electron displacement in the conjugation chain. The acceptance (or loss) of a proton by an indicator molecule, leading to the intensification of electron-donor or electron-acceptor ability of the substituents, is accompanied with the deepening and intensification of colour. This is manifested most clearly during the dissociation of such electron-donor substituents as —OH, —SH, —NH_2 and the acceptance of protons by such electron-acceptor substituents as

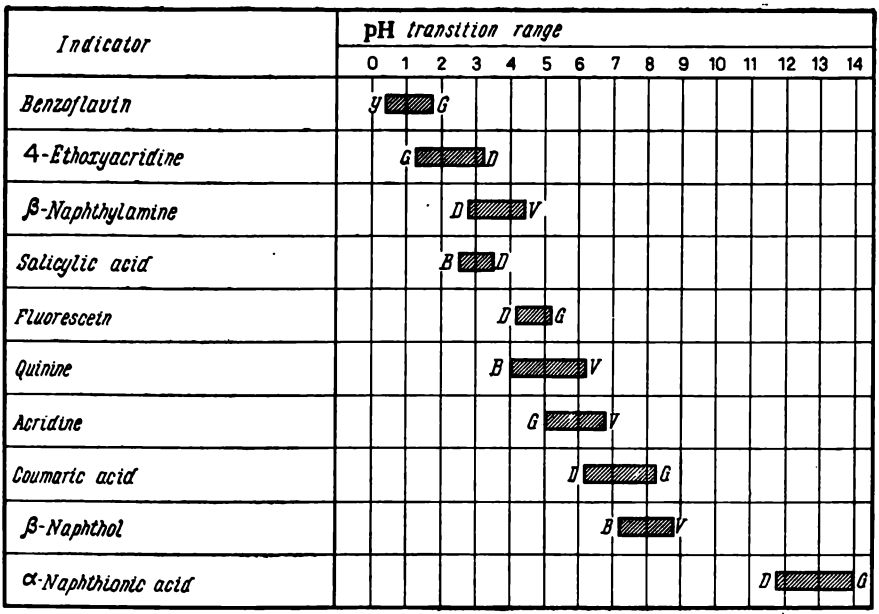


The foregoing should be explained by a classical example of a widely known indicator of phenolphthalein:





C= colourless, D=dark blue, O=orange, R=red, V=violet, Y=yellow



B=blue, D=dark blue, G=green, V=violet, Y=yellow

The colour of any colour indicator changes in a certain pH-value range known as indicator colour-change interval, which is calculated by the formula:

$$pH = pK - \log \frac{c_{a.\,ph}}{c_{b.\,ph}}$$

where K = constant of indicator dissociation; for example the pK of phenolphthalein is 9.7.

The shade of colour assumed by an indicator in a solution depends on the ratio [HIn]/[In].

Experiment 52. Colour Transition of Methyl Orange

The smooth change in the indicator colour from one form to another may be demonstrated by a special prism

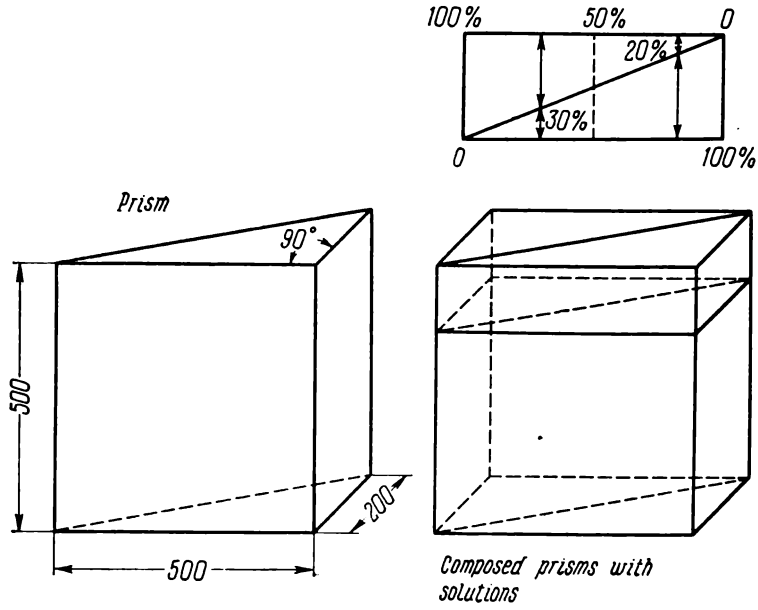
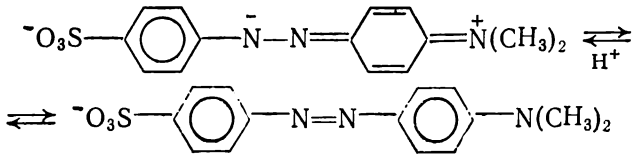


Fig. V-2. Demonstration of the colour change of an indicator by prisms

made of plexiglas (Fig. V-2). As indicator, use should be made of methyl orange, which is one of the most com-

monly used indicators in analytical practice



Reagents

Methyl orange, 1 per cent solution.
Hydrochloric acid, concentrated.
Sodium hydroxide, 2 *M* solution.

Procedure. Fill the prisms with water and to each add 20 ml of methyl orange solution. To one of them, add concentrated hydrochloric acid until the solution becomes red. To the other prism, add a sodium hydroxide solution until the solution becomes yellow. Put the two prisms on a sheet of white paper on the table separately at first, and at the lecture combine them so that they would form a right parallelepiped. In looking at the combined prisms sideways, a smooth colour change of the indicator may be observed from yellow through orange to red.

Note. The colour change of other indicators, such as congo red, may also be similarly shown.

Experiment 53. Determination of the pH of a Solution by a Universal Indicator

Universal indicators, which are mixtures of several indicators, change their colour at different pH values in a wide range of the latter. Mixed indicators are mixtures of either two indicators with close p*K* values or an indicator with a dye that is insensitive to a change in the pH. An example of a mixed indicator is a mixture of cresol red (0.1 per cent solution) and thymol blue (0.1 per cent solution) taken in the ratio of 1 to 3, making it possible to very accurately mark pH 8.3, which conforms to a sodium bicarbonate solution. Mixed indicators are used in titration when at a certain pH value it is necessary to make the colour change more contrasting: they may be useful

in the titration of coloured solutions and in titration in artificial light, when colours are poorly distinguishable.

Reagents

A universal indicator. 0.05 g of thymol blue, 0.012 g of methyl red, 0.06 g of bromothymol blue and 0.1 g of phenolphthalein are dissolved in 100 ml of ethanol. 0.05 *N* sodium hydroxide solution is added until the appearance of a green colour, and then the solution is diluted to 200 ml with water.
Hydrochloric acid, 0.01 *N* solution (pH $\approx$ 2).
Ammonium chloride, 0.1 *N* solution (pH $\approx$ 5), saturated solution (pH $\approx$ 6).
Sodium chloride, 1 *M* solution (pH $\approx$ 7).
Sodium hydrophosphate, 0.1 *N* solution (pH $\approx$ 8).
Sodium carbonate, 0.1 *N* solution (pH $\approx$ 10).

Procedure. Take six cylinders and in each of them put 200 ml of the above-mentioned solutions with a certain pH value. At the lecture, add 5-6 drops of indicator solution to each cylinder. A spectrum is observed: red (pH $\approx$ 2), orange (pH $\approx$ 5), yellow (pH $\approx$ 6), green (pH $\approx$ 7), dark blue (pH $\approx$ 8) and violet (pH $\approx$ 10). In the seventh cylinder, put a reference solution with one of the given pH values (the best is pH $\approx$ 8). Note that it is necessary to determine the pH. Add 5-6 drops of the indicator, stir, and put the cylinder next to the cylinder with a solution of similar colour.

Note. The experiment may be carried out beforehand and the prepared coloured solutions in cylinders with labels indicating the pH value may be put on the table.

Experiment 54. Effect of Temperature on the Colour of Phenolphthalein

The water dissociation constant greatly depends on temperature; hence, pK_w is 14.2 at 18° C and 12.2 at 100° C. In dilute alkaline solutions, pOH does not change on heating, while pH diminishes. Therefore phenolphthalein,

which has a colour-change range at pH = 8.3 ÷ 10.0, becomes decoloured on heating.

Reagents
Sodium hydroxide, 0.01 *N* solution.
Phenolphthalein, 0.1 per cent ethanol solution.

Procedure. Take two 0.5-litre heat-resistant beakers and in each of them put 250 ml of water and 2.5 ml of sodium hydroxide solution. At the lecture, add 5 drops of the indicator to each beaker. The solutions become red. Heat one beaker until its contents boil. The colour disappears.

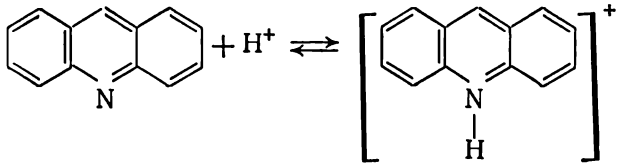
Fluorescent Indicators

It is convenient to use fluorescent indicators for determining the pH of solutions or the equivalence points in the case of acid-base titration of turbid or coloured solutions (wine, vegetable and berry juices, and products of organic synthesis). The ionization of the functional groups of indicator molecules is accompanied with the intensification or weakening of the electron-donor or electron-acceptor properties of substituents, leading to the displacement of emission spectra and a change in fluorescence colour. Many fluorescent indicators are characterized by the fact that when an indicator molecule is excited, its acid and base properties become more pronounced in comparison with an unexcited molecule; ionization constants and the indicator range change.

Experiment 55. Titration of Coloured Acid Solutions in the Presence of Acridine

Acridine is a weak organic base which in the excited state has greater proton-acceptor power than in the unexcited state. The acceptance of a proton to an acridine molecule causes the bathochromic shift of the luminescence spectrum; therefore, under the action of ultraviolet radiation, acridine solutions have different luminescence, depending on the pH of the medium; violet in an alkaline medium (λ_{max} = 425 nm) and bluish-green in an acid

medium (λ_{max} = 478 nm). The transition range is 5.0-6.6:



Equipment and Reagents

Luminescent lamp with a case of special structure (Fig. V-3).

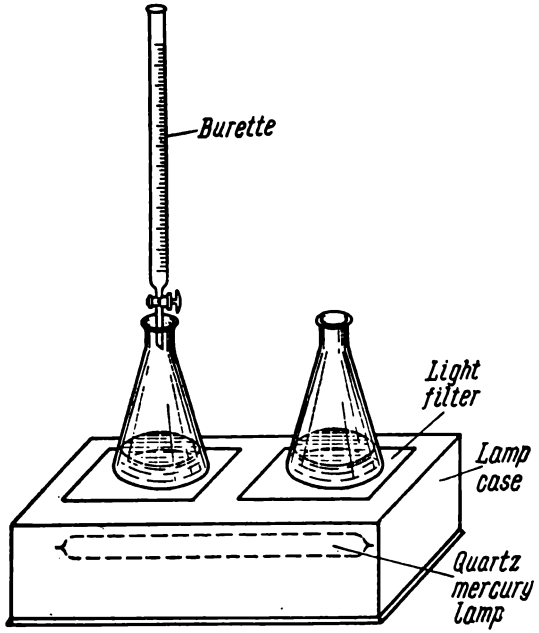


Fig. V-3. Instrument for titration with fluorescent indicators

Acridine, 0.02 per cent solution. 0.2 g of acridine is dissolved in 100 ml of water which contains 1 ml of concentrated hydrochloric acid.
Hydrochloric acid, 0.1 *N* solution.
Sodium hydroxide, 0.1 *N* solution.
Black India ink.

Procedure. Take three conical 300-ml flasks and in each of them put 100 ml of water, 5 ml of 0.1 *N* hydrochloric

acid solution and 1 ml of acridine solution. Put two flasks in the path of ultraviolet radiation. Darken the auditorium and switch off the electric light. In the dark, the solutions have a bluish-green luminescence. Keep one solution for reference, and to another one pour 0.1 *N* sodium hydroxide solution from a burette. At the equivalence point, the blue luminescence sharply changes to a violet luminescence.

To the third flask add, in an ordinary light, 3-4 drops of India ink and stir. Draw the attention of the audience to the fact that titration is impossible with colour indicators in such a solution. Switch off the light and titrate the solution with alkali until the luminescence colour changes.

Chemiluminescent Indicators

In acid-base titrations, chemiluminescent indicators are also used. Under the action of a chemical reaction, the molecules of a reaction product become excited; as a result, light is emitted (see Chapter II). The chemiluminescence of indicators occurs only at a certain pH-value. Most chemiluminescent indicators (luminol, lucigenin) are capable of passing over to an excited state only in an anion form, i.e., in an alkaline medium. In an acid medium, a luminescence does not occur even in the presence of a catalyst.

Experiment 56. Acid Titration in the Presence of Luminol

Depending on the pH and the solvent, luminol (H_2L) may be in a solution in different forms:

$$\underset{pH<1.3}{H_3L^+} \rightleftarrows \underset{pH=1.3\div6.7}{H_2L} \rightleftarrows \underset{pH=6.7\div14}{HL^-} \rightleftarrows \underset{pH>14}{L^{2-}}$$

At pH $\approx$ 8 in the presence of a catalyst (potassium ferricyanide), an intense green luminescence (λ_{max} = 460 nm) is observed.

Reagents

Luminol.

Potassium ferricyanide, 10 per cent solution.

Hydrogen peroxide, 30 per cent solution.
Sodium hydroxide, 30 per cent solution.
Hydrochloric acid, concentrated.

Procedure. In a large flat-bottomed 3-litre flask, put 2 litres of water, 10 ml of potassium ferricyanide solution and 10 ml of concentrated hydrochloric acid. At the lecture, add 20 ml of hydrogen peroxide solution and 20-30 mg of solid luminol (or lucigenin). Switch off the light and pour in 20 ml of alkaline solution in the dark. An intense green luminescence appears.

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CHAPTER VI

Equilibrium in heterogeneous systems. Precipitate and its properties

In analytical chemistry, the heterogeneous systems liquid-solid and liquid-liquid are of the greatest importance.

Equilibrium in a heterogeneous system obeys the law of mass action and is quantitatively characterized by equilibrium constants, which are known as extraction constant (K_{ex}) for the liquid-liquid system, and solubility product (K_{sp}) for the solution-precipitate system. Like equilibrium in a homogeneous system, equilibrium in a heterogeneous system is characterized by thermodynamic, concentration and conditional equilibrium constants [1].

For precipitate-solution equilibrium:

$$AB\downarrow \rightleftarrows A^+ + B^-$$

$$K_{sp}^t = a_{A^+} \cdot a_{B^-}; \quad K_{sp}^c = \frac{K_{sp}^t}{f_{A^+} \cdot f_{B^-}}$$

$$K_{sp}^{con} = \frac{K_{sp}^t}{f_{A^+} \cdot f_{B^-} \cdot \alpha_{A^+} \cdot \alpha_{B^-}}$$

where K_{sp}^t, K_{sp}^c, K_{sp}^{con} = thermodynamic, concentration, conditional solubility products;
f = activity coefficient;
α = side reaction coefficient.

For liquid-liquid equilibrium, such as equilibrium between water and organic solvent, which is water-immiscible organic solvent:

$$M_{aq}^{n+} + nHL_{org} \rightleftarrows ML_{n\,org} + nH_{aq}^+$$

$$K_{ex} = \frac{[ML_n]_{org} \cdot [H^+]_{aq}^n}{[M^{n+}]_{aq} \cdot [HL]_{org}^n}$$

DISTRIBUTION OF A SOLUTE BETWEEN TWO IMMISCIBLE LIQUIDS

The property of substances to distribute between two immiscible liquids (solvent extraction) is widely employed in analytical chemistry. Solvent extraction is used for separating elements and concentrating element traces [2].

It is expedient to show some data on the separation of elements by extraction with the utilization of organic reagents, such as the pH of extraction of metal hydroxyquinolinates, metal dithizonates, and so forth. The pH values of extraction of metal hydroxyquinolinates by chloroform are given below:

Ion	Extraction pH	Ion	Extraction pH
Mo^{VI}	1.6-5.6	Al^{3+}	> 4.6
Fe^{3+}	> 2.0	Zn^{2+}	4.6-14
Cu^{2+}	2.8-12	Mg^{2+}	> 10.2
Ni^{2+}	4.5-9.5	Co^{2+}	> 6.8

Experiment 57. Distribution of Iodine Between Chloroform and Water

Molecular iodine is well soluble in organic solvents (chloroform, carbon tetrachloride, alcohols) and slightly soluble in water. The partition constant of iodine is:

$$K_d = \frac{[I_2]_{CHCl_3}}{[I_2]_{H_2O}} = 180$$

Reagents

Iodine, 0.2 per cent solution. 0.2 g of crystal iodine and 1 g of potassium iodide are dissolved in 100 ml of water.

Chloroform.

Procedure. In a cylinder, put 10 ml of iodine solution and 400 ml of water. At the lecture, add 120 ml of chloroform and strongly shake the mixture several times (use a protective screen!). Observe the separation of a colourless aqueous phase and a violet organic phase against a white screen.

Experiment 58. Extraction of Cobalt Thiocyanate by Isoamyl Alcohol

A complex of cobalt with thiocyanate ions is extracted by oxygen-containing organic solvents (alcohols, ethers). This is used for detecting cobalt, separating it from other elements and increasing the sensitivity of determination of cobalt (by 20 times on extraction with an equal volume of an organic solvent):

$$[Co(NCS)_n(H_2O)_{6-n}]^{(n-2)-}_{aq} + (n-2)\,H^+_{aq} + mH_2O + lS_{org} \rightleftarrows$$
$$\rightleftarrows H_{(n-2)}(H_2O)_mS_l\,[Co(NCS)_n(H_2O)_{6-n}]_{org}$$

Reagents

Cobaltous chloride, 0.1 per cent solution.
Ammonium thiocyanate, 20 per cent solution.
Isoamyl alcohol.

Procedure. In a cylinder, put 10 ml of cobalt chloride solution and 100 ml of water. At the lecture, add 100 ml of ammonium thiocyanate solution. The solution becomes slightly pink. Add 70 ml of isoamyl alcohol and shake (use a protective screen!). The organic layer becomes dark blue.

Experiment 59. Extraction of Bismuth Iodide Complex

The bismuth ion forms several complexes with iodide ions. In solutions containing an excess of iodide ions, the anion $[BiI_4]^-$ of orange colour is formed; this anion is extracted from acid solutions by oxygen-containing organic solvents in the form of an acido complex:

$$[BiI_n]^{(n-3)-}_{aq} + (n-3)\,H^+_{aq} + mH_2O + lS_{org} \rightleftarrows$$
$$\rightleftarrows H_{(n-3)}(H_2O)_mS_l\,[BiI_n]_{org}$$

The given pattern is simplified, since aqueous solutions contain complex hydroxy aquo-ions of bismuth.

Under the action of oxidizing agents, such as atmospheric oxygen, the iodide complex of bismuth may be destroyed with the liberation of free iodine. This may be

avoided if a reducing agent (ascorbic acid, sulphite) is added to the solution.

Reagents
Bismuth nitrate, solution in 0.5 *N* nitric acid that contains 1 mg of Bi in 1 ml.
Potassium iodide, 2 per cent solution.
Mixture of amyl acetate and isoamyl alcohol (1 : 1).
Sulphuric acid, 5 *M* solution.
Ascorbic acid.

Procedure. In a cylinder, put 2 ml of bismuth nitrate solution, 50 ml of sulphuric acid and 150 ml of water. At the lecture, add 30 ml of potassium iodide solution and 30-40 mg of ascorbic acid. The solution becomes yellow. Add 100 ml of a mixture of amyl acetate and isoamyl alcohol, and shake (use a protective screen!). The organic layer becomes orange.

Experiment 60. Extraction of the Vanadic Ion by *N*-Benzoylphenylhydroxylamine [3]

The vanadic ion forms with BPHA a violet-red complex having the composition $V_2O_3(C_{13}H_{10}O_2N)_4$, which is extracted by chloroform [4].

Reagents
Ammonium vanadate, 0.1 per cent solution.
N-Benzoylphenylhydroxylamine, 0.1 per cent chloroform solution.
Hydrochloric acid, 6 *M* solution.

Procedure. In a cylinder, put 15 ml of ammonium vanadate solution, 150 ml of water and 50 ml of hydrochloric acid solution. At the lecture, add 100 ml of a chloroform solution of *N*-benzoylphenylhydroxylamine and shake (use a protective screen!). The organic layer becomes violet-red.

Note. Experiments 6, 141, 164-167 may also be demonstrated.

SOLID-SOLID EQUILIBRIUM

Experiment 61. Interaction of the Precipitates of Lead Sulphate and Zinc Sulphide

The solubility of lead sulphide is considerably less than the solubility of lead sulphate and zinc sulphide:

$$-\log K_{sp_{PbS}} = 28.96; \quad -\log K_{sp_{PbSO_4}} = 7.66$$

$$-\log K_{sp_{ZnS\beta}} = 22.92; \quad -\log K_{sp_{ZnS\alpha}} = 25.16 \ (25^\circ\,C, \ \mu \to 0)$$

Therefore, when the white precipitates of $PbSO_4$ and ZnS interact with one another, black lead sulphide is slowly formed:

$$\underset{\text{white}}{ZnS\downarrow} + \underset{\text{white}}{PbSO_4\downarrow} \rightleftarrows \underset{\text{black}}{PbS\downarrow} + ZnSO_4$$

Procedure. Immediately before the lecture, prepare the precipitates of lead sulphate and zinc sulphide, filtering them and washing them with water. Put the precipitates into two cylinders, and add to each of them 150 ml of water and shake. At the lecture, pour off both suspensions and observe the slow darkening of the mixture against a white screen. In several minutes, the precipitate becomes black.

Note. A similar experiment may be demonstrated by using freshly-precipitated cadmium sulphide and lead sulphate ($CdS - \log K_{sp} = 25.76$, 25° C, $\mu = 1$).

$$\underset{\text{yellow}}{CdS\downarrow} + \underset{\text{white}}{PbSO_4\downarrow} \rightleftarrows \underset{\text{black}}{PbS\downarrow} + CdSO_4$$

PRECIPITATE-SOLUTION EQUILIBRIUM

Precipitate Formation

In gravimetric analysis, it is necessary to obtain pure and well-filtering precipitates, i.e., coarse-crystal and possibly homogeneously-dispersed precipitates. The granulometric composition is determined by the relative rate of crystal nucleation and the growth of crystal nuclei. The coefficient of the precipitate form N, which characterizes

the number of crystal nuclei, is calculated by the equation:

$$N = K\frac{P-S}{S}$$

where P = initial concentration of the ion in the solution;
S = compound solubility;
K = constant that depends on the solvent and the nature of the compound [5, 6].

The lesser the N, the greater is the coarse-crystal precipitate. The following factors that influence the value of

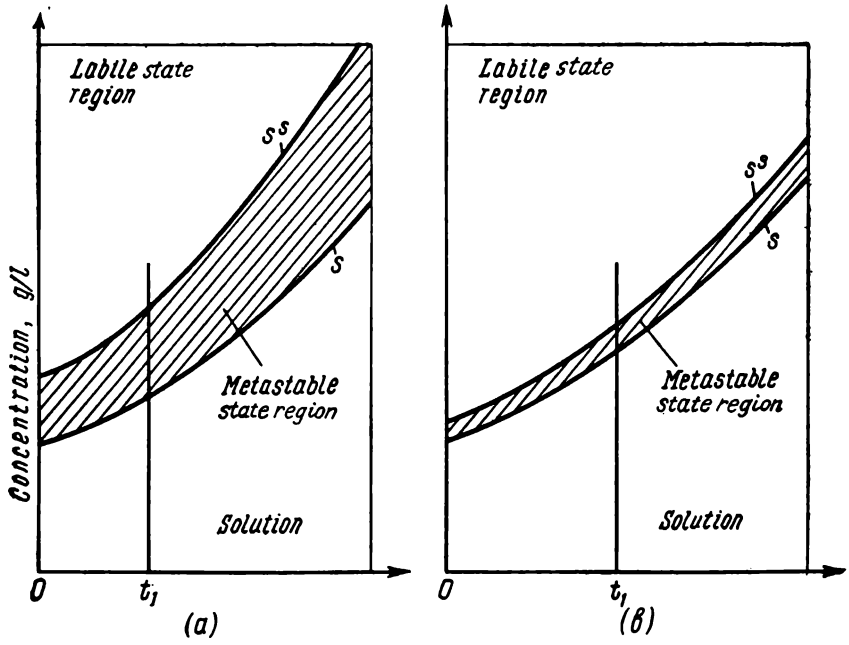


Fig. VI-1. Dependence of the solubility (S) and supersaturation (S^s) of precipitates on temperature for barium sulphate (*a*) and silver chloride (*b*)

N may be indicated: dilution of solutions, temperature (Fig. VI-1), stirring, change in pH (Fig. VI-2), complex formation, salt effect, and the presence of surfactants. An especially effective method of obtaining coarse-crystal precipitates is precipitation from a homogeneous system (method of originating reagents) [7, 8]. Such precipitation

may be effected either by gradually reducing solubility, which is ensured by a gradual rise in the pH as a chemical reaction slowly proceeds together with the binding of hydrogen ions, or by gradually increasing the concentration of precipitant ions, or of an ion being determined, by a reaction that proceeds with the gradual formation of

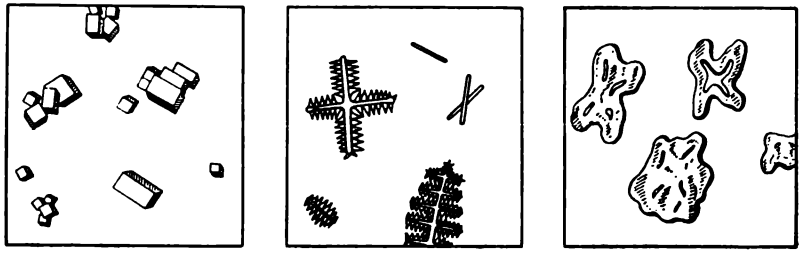


Fig. VI-2. Form of barium sulphate crystals obtained at different pH of precipitation

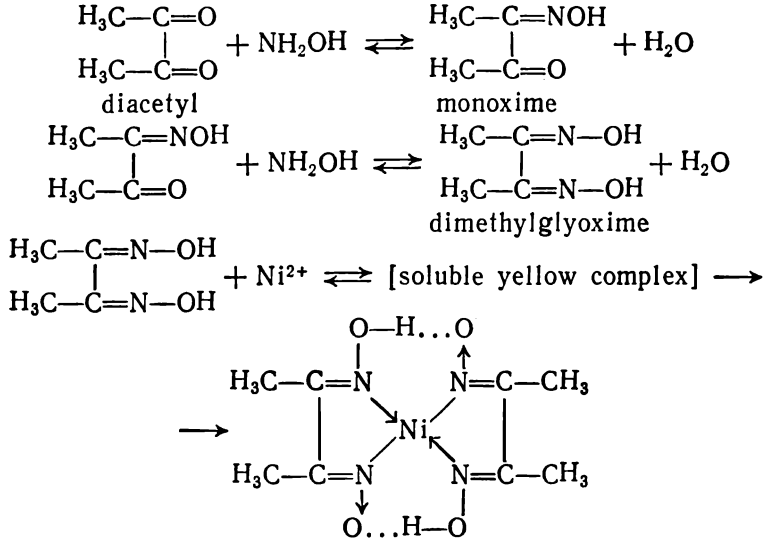
these ions. Examples of the method of originating reagents is precipitation of cobalt sulphide from a pyridine solution [9], precipitation of nickel dimethylglyoximate that has been synthesized during the reaction of precipitation by the reagent [10], and so forth.

Method of Originating Reagents (Homogeneous Precipitation)

Experiment 62. Precipitation of a Nickel Ion by Dimethylglyoxime

Dimethylglyoxime may be synthesized from diacetyl and hydroxylamine in a solution being analyzed. A reagent gradually "originates" in small concentrations in the solution; this promotes the formation of a sufficiently coarse-crystal precipitate of nickel dimethylglyoximate. The formation of the compounds may be described by the fol-

lowing simplified pattern [10]:



The precipitate of nickel dimethylglyoximate is formed slowly. The induction period depends on reagent concentration and the pH of the solution:

pH	7.9	7.7	7.5	7.3	7.1
Induction period, min .	2	4	6	8	12

Reagents

Solution A. 5 g of ammonium chloride, 3 g of hydroxylamine and 0.38 g of nickel sulphate are dissolved in 200 ml of water; 25 per cent ammonia solution is added until the pH is 7.5, and then diluted to 400 ml with water.

Solution B. 0.6 g of diacetyl is dissolved in 400 ml of water.

Solution C. 5 g of ammonium chloride, 5 ml of 25 per cent ammonia solution and 0.38 g of nickel sulphate are dissolved in 400 ml of water.

Solution D. 0.1 per cent dimethylglyoxime solution in a mixture of ethanol and water (1 : 1).

Procedure. Put solutions *A* and *C* in 1-litre cylinders. At the lecture, add solution *D* to solution *C* and stir. A bulky loose precipitate of nickel dimethylglyoximate is immediately formed. To solution *A*, add solution *B* and

stir. The solution remains colourless and transparent. Put a white screen behind the cylinder. In several minutes, a yellow colour appears; its intensity grows, and finally a pink precipitate of nickel dimethylglyoximate in the shape of long needles is formed.

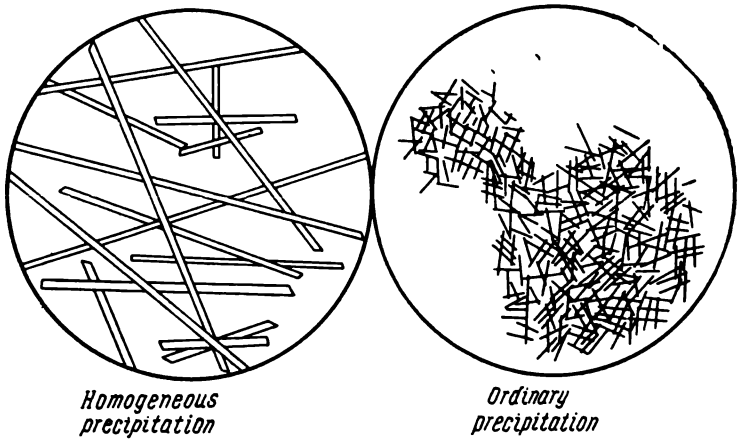
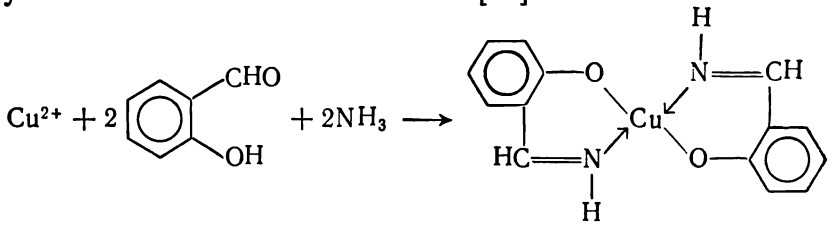


Fig. VI-3. Precipitate of nickel dimethylglyoximate obtained by homogeneous precipitation and by the ordinary method

Note. Immediately after the experiment, photographs of nickel dimethylglyoximate precipitate produced by the ordinary method and by the method of originating reagents (Fig. VI-3) may be shown to the audience.

Experiment 63. Precipitation of the Copper Ion by Salicylalimine

In precipitating the copper ion by salicylalimine, not the prepared reagent, but its components (salicylaldehyde and ammonia) may be added, and the reagent will be synthesized in the solution itself [11]:



Lustrous scales with a silver tint are formed.

Reagents
Salicylaldehyde, 2 per cent solution.
Cupric sulphate, 1 per cent solution.
Ammonia, 20 per cent solution.
Phenolphthalein, 1 per cent ethanol solution.

Procedure. In a 0.5-litre beaker, put 20 ml of copper sulphate solution and 250 ml of water. Heat the solution to boiling and add 40 ml of salicylaldehyde solution, 10 drops of phenolphthalein solution and then ammonia solution until a pink colour appears. Heat the solution again to boiling and observe the appearance of a precipitate.

Experiment 64. Precipitation of Barium Sulphate by Dimethyl Sulphate

On hydrolizing, dimethyl sulphate forms sulphate ions:

$$(CH_3)_2SO_4 + 2H_2O \rightleftarrows 2CH_3OH + H_2SO_4$$

This is used for producing coarse-crystal sulphates of alkali earth metals ($-\log K_{sp_{BaSO_4}} = 10$; 25° C, $\mu \to 0$).

Reagents
Barium chloride, 0.5 per cent solution.
Dimethyl sulphate.

Procedure. In a 1-litre beaker, put 5 ml of barium chloride solution, 400 ml of water and 20 ml of dimethyl sulphate. Draw the attention of the audience to the absence of a precipitate. With a burner, heat the beaker containing the solution. Observe the formation of a white precipitate against a black screen.

Note. The audience may be shown microphotographs of barium (or calcium) sulphate crystals produced by the method of originating reagents and by the ordinary method.

Perfection of the Crystal Structure of a Precipitate

On standing, a precipitate undergoes changes. In this case, a metastable modification assumes another, more stable form; there occurs recrystallization, druse formation, thermal ageing, and "Ostwald ripening" [12].

Experiment 65. "Ostwald Ripening" of a Precipitate

Among the processes that occur with a precipitate is the dissolution of fine and the growth of coarse particles, i.e., "Ostwald ripening". Fine crystals have more active sites (facets, angles) on their surface and higher surface energy; consequently, they are more soluble than coarse crystals, and dissolve more rapidly. As a result, the average size of crystals increases in the course of time (Table VI-1) [13]. It should be noted that the dependence of solubility on the size of particles is more clearly defined in precipitates with a high free surface energy (barium sulphate, lead chromate, etc.) than in precipitates with a low surface energy (silver chloride).

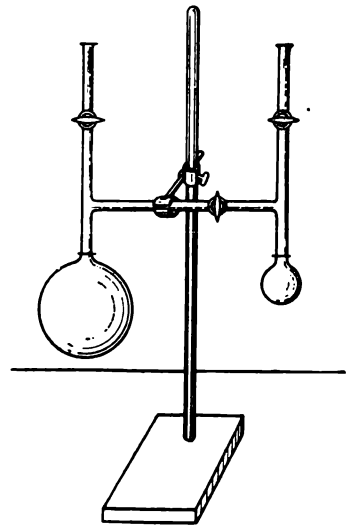


Fig. VI-4. Instrument for demonstrating the Ostwald ripening

A decrease in the overall surface may be demonstrated by Ostwald's experiment [14].

Table VI-1

SOLUBILITY OF LEAD CHROMATE AS DEPENDENT ON PARTICLE SIZE

Compound	Shaking time, min	Calculated particle radius, μm	Solubility (mol/l)·10⁴
Aged	1	—	1.30
	6	—	1.28
	1440	0.45	1.28
Freshly-precipitated, consisting of fine particles	1	0.086	2.10
	5	—	1.85
	20	0.28	1.41
	1440	0.30	1.24

Equipment and Reagents

Double T-tube made of glass tubes with cocks (Fig. VI-4).

Soap solution. 10 g of oleic acid is dissolved in a sodium hydroxide solution; hydrochloric acid is added to the solution obtained until the appearance of turbidity, and then 25 g of glycerin is added and the solution is diluted to 100 ml with water.

Procedure. From the lower opening of every tube, blow out a soap bubble of different size (in this case, the coupling cock is closed). Close the upper cocks, and open the coupling cock. In this case, a large bubble increases in size at the expense of the smaller one.

Note. If the solution is coloured with eosin, the soup bubble will be seen at a great distance.

Washing of Precipitates

Surface-adsorbed substances are removed from the precipitate by washing. Repeated washing by small portions of a wash liquid is most effective. The contents of foreign matter c_n that remains on the precipitate after n washings may be calculated by the formula

$$c_n = \left(\frac{V_0}{V + V_0}\right)^n c_0$$

where V_0 = amount of the wash liquid that remains in the pores of the precipitate;
V = amount of each portion of the wash liquid;
c_0 = initial concentration of foreign matter.

Experiment 66. Washing of Coloured Sand with Water

Reagents
Bank sand, white.
Indigo carmine, 5 per cent solution.
Potassium permanganate, 0.2 per cent solution.

Procedure. Take two 1-litre beakers and in each of them put 100 g of bank sand. Wet the sand with 50 ml of indigo carmine solution or of potassium permanganate solution. Wash the sand in one beaker by decantation with five portions of water, each portion being 100 ml. In the other beaker, wash the sand at once with 500 ml of water.

Compare the colour of the sand in both beakers and the colour of wash liquids [14]. The sand in the first beaker is practically uncoloured.

Dissolution of Precipitates

The solubility of precipitates depends on temperature, the nature of a solvent, ionic strength, and the presence of common ions and side reactions, and also on the structure of a precipitate and the degree of its dispersion. Graphs may be shown to illustrate the effect of some factors on solubility (Figs. VI-5, VI-6). In the same sol-

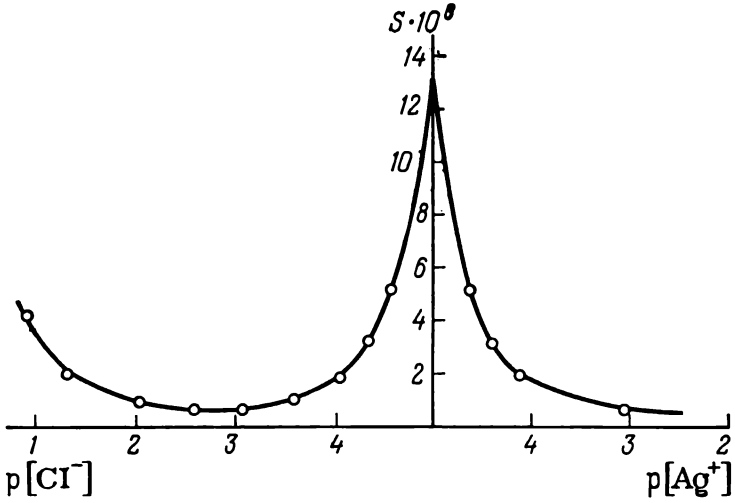


Fig. VI-5. Dependence of the solubility of silver chloride on the concentration of common ions

vent, the effect of physical factors is inconsiderable in comparison with chemical ones, mainly such factors as side reactions (complex formation, interaction of precipitate ions with hydrogen ions).

The coefficient of a side (competing) reaction of complex formation with certain precipitate ions may be calculated by the formula:

$$\alpha = \frac{1}{\sum_{0}^{N} \beta_n a^n}$$

where α = side reaction coefficient;
a = equilibrium ligand concentration;
β_n = overall stability constant.

Experiment 67. Dissolution of Mercury Iodide with the Formation of Mercury (II) Complexes

The mercuric ion forms with the iodide ion complexes among which only mercuric iodide HgI_2 is slightly soluble:

$$Hg^{2+} \overset{I^-}{\rightleftarrows} [HgI]^+ \overset{I^-}{\rightleftarrows} HgI_2\downarrow \overset{I^-}{\rightleftarrows} [HgI_3]^- \overset{I^-}{\rightleftarrows} [HgI_4]^{2-}$$

colourless red colourless colourless

$\log K_1 = 12.87$ $\log K_2 = 10.95$ $\log K_3 = 3.78$ $\log K_4 = 2.23$

(25° C, $\mu = 0.5$)

The complex ions $[HgI]^+$, $[HgI_3]^-$ and $[HgI_4]^{2-}$ are soluble; therefore, the precipitate is dissolved in both an excess of mercuric ions and an excess of iodide ions.

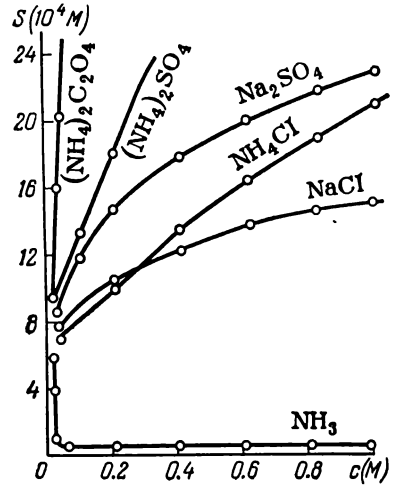


Fig. VI-6. Dependence of the solubility of magnesium-ammonium phosphate on the concentration of different electrolytes

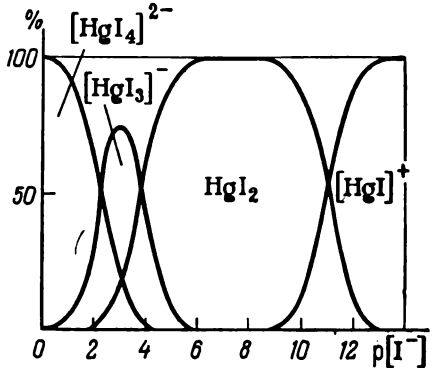


Fig. VI-7. Distribution of complex ions of mercury iodide

A diagram of the regions where complex forms of mercury iodide exist may be shown (Fig. VI-7).

Reagents

Mercuric nitrate, 1 per cent solution in 0.1 *N* nitric acid solution.

Potassium iodide, 10 per cent solution.

Procedure. In a cylinder, put 50 ml of mercury nitrate solution and 200 ml of water. At the lecture, add a potassium iodide solution in the following manner: first, add with a pipette 1-2 drops of potassium iodide solution and shake the cylinder. Draw the listeners' attention to the fact that the red precipitate of mercuric iodide HgI_2 formed is dissolved in an excess of mercury nitrate. Add some more drops of potassium iodide solution, observing the dissolution of the precipitate. Then, add 10 ml of potassium iodide solution. A red precipitate is formed. Add the excess of potassium iodide solution and observe the dissolution of the precipitate.

Note. The experiment may be somewhat modified: produce a mercury iodide precipitate and pour the solution with the precipitate into two cylinders. To one cylinder, add an excess of mercury nitrate solution, and to the other, an excess of potassium iodide solution. The precipitate is dissolved in both cylinders.

Experiment 68. Dissolution of Calcium Fluoride by Complex Formation

Freshly-precipitated calcium fluoride ($-\log K_{sp} = 10.4$) is insoluble in acids, but soluble in aluminium salts due to the formation of stable fluoride complexes $[AlF_2]^+$ ($\log \beta_2 = 11.17$; 25° C, $\mu = 0.5$)

$$CaF_2\downarrow + Al^{3+} \rightleftarrows [AlF_2]^+ + Ca^{2+}$$

Calcium fluoride is soluble also in EDTA due to the formation of calcium complexonate ($\log \beta_1 = 10.59$, 25° C, $\mu = 0.1$)

$$CaF_2\downarrow + H_2Y^{2-} \rightleftarrows [CaY]^{2-} + 2HF$$

Reagents

Calcium chloride, 1 per cent solution.

Ammonium fluoride, saturated solution.

Aluminium chloride, saturated solution.

Acetic acid, 30 per cent solution.

Procedure. In a 500-ml beaker, put 60 ml of calcium chloride solution. At the lecture, add 20 ml of ammonium fluoride solution. A white precipitate of calcium fluoride is formed. Add 50 ml of acetic acid; the precipitate does not dissolve. Add 200 ml of aluminium chloride solution, stir and slightly heat. Observe the dissolution of the precipitate against a black screen.

Experiment 69. Effect of a Common Ion on the Solubility of Barium Sulphate

Reagents

Barium chloride, $7 \cdot 10^{-4}$ *M* and 5 per cent solutions.
Sulphuric acid, $7 \cdot 10^{-4}$ *M* solution.
Ammonium sulphate, 5 per cent solution.

Procedure. In a cylinder, put 250 ml of $7 \cdot 10^{-4}$ *M* solution of barium chloride. At the lecture, add an equal amount of $7 \cdot 10^{-4}$ *M* solution of sulphuric acid and stir. The formation of a barium sulphate precipitate is not observed. Divide the mixture into three equal parts by pouring it into cylinders. To the first part, add 20 ml of 5 per cent barium chloride solution, to the second, 20 ml of 5 per cent ammonium sulphate solution, and keep the third part for reference. In the first two cylinders, great turbidity is observed, while in the last cylinder the precipitate does not appear for a considerable time.

COPRECIPITATION

A precipitate may be contaminated as a result of coprecipitation, simultaneous precipitation and postprecipitation. Simultaneous precipitation is the simultaneous formation of two precipitates and more. In postprecipitation, a pure precipitate is first formed, and an impurity is separated on standing. Coprecipitation consists in the capture of impurities from the solution during precipitation [15-17].

In analytical chemistry, coprecipitation as a rule plays a negative role; this gives rise to errors in gravimetri-

cally determining elements, on the one hand, and to a loss of the element being coprecipitated, on the other. However, coprecipitation is occasionally used in analysis, for instance, for concentrating microimpurities and increasing the sensitivity of detecting and determining ions (Table VI-2) [18].

Table VI-2

CONCENTRATION OF SOME IONS BY COPRECIPITATION

Ion being concentrated (microcomponent)	Carrier (macrocomponent)	Minimum concentration of a microcomponent, g/l
Ni^{2+}	$Mg(OH)_2$	10^{-6}
UO_2^{2+}	$Fe_2O_3 \cdot xH_2O$	$1.5 \cdot 10^{-6}$
Ti^{IV}	$Al_2O_3 \cdot xH_2O$	10^{-6}
Sn^{IV}	$Fe_2O_3 \cdot xH_2O$	10^{-6}
Au^{III}	PbS	10^{-9}
Pu^{IV}	$La_2(C_2O_4)_3$	10^{-9}

Coprecipitation includes adsorption and occlusion. Adsorption is the precipitation of impurities on the surface of a precipitate due to the non-equivalence of the electrostatic field of an ion inside the crystal lattice and on the surface. Occlusion is the internal capture of an impurity by the entire volume of the precipitate particles. By the capture mechanism, occlusion is classified into internal adsorption and the inclusion of mother liquor. The isomorphous displacement of ions, and also the formation of solid solutions and chemical compounds may occur.

Adsorption

When some ions are precipitated, amorphous, gelatinous precipitates with a highly-developed surface that adsorb ions from the solution are often formed. To give a clear picture of the greatness of a precipitate surface, it is necessary to show an illustration and a table of the dependence of a precipitate surface on the degree of particle dispersion (Fig. VI-8, Table VI-3) [19].

Table VI-3

DEPENDENCE OF THE PRECIPITATE SURFACE ON THE DEGREE OF PARTICLE DISPERSION

Rib length, mm	Number of cubes	Total surface, cm^2	Rib length, mm	Number of cubes	Total surface, cm^2
10	1	6	10^{-3}	10^{12}	$6 \cdot 10^4$
1	10^3	60	10^{-4}	10^{15}	$6 \cdot 10^5$
10^{-1}	10^6	$6 \cdot 10^2$	10^{-5}	10^{18}	$6 \cdot 10^6$
10^{-2}	10^9	$6 \cdot 10^3$	10^{-6}	10^{21}	$6 \cdot 10^7$

The amount of adsorbed impurities depends on the precipitate surface, impurity concentration in a solution, temperature, and so forth.

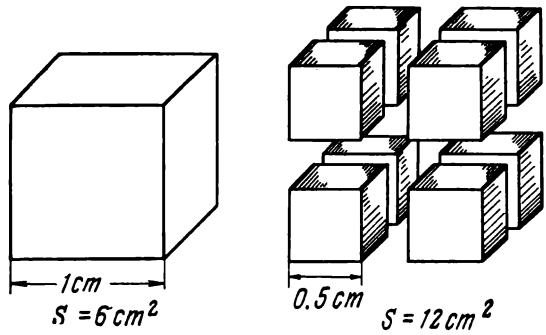


Fig. VI-8. Dependence of the precipitate surface on the degree of particle dispersion

The dependence of adsorption on impurity concentration is shown in Fig. VI-9.

Experiment 70. Adsorption of Methylene Blue by the Silicic Acid Gel

For demonstrating the adsorption process, the most suitable adsorbent is the gel of silicic acid, i.e., silica gel, which has a large surface (100 m^2/g) and carries a negative charge. Coloured inorganic ions are scarcely suitable

for observing the adsorption process, since their colour is not sufficiently intense. The adsorption of large intensely-coloured cations of organic dyes is more graphic; these dyes are retained by silica gel quite strongly, and they are difficult to wash out with water. Methylene blue, and also methyl violet and rhodamine dyes, may be used.

Equipment and Reagents

Chromatographic column having a height of 40 cm and a diameter of 3 cm, and filled with silica gel (Fig. I-7).

White silica gel, coarse-grained.

Methylene blue, 0.1 per cent solution.

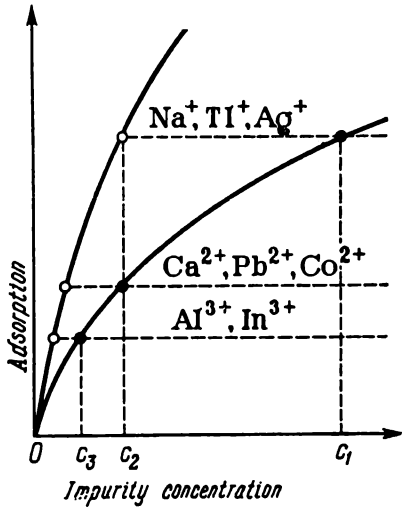


Fig. VI-9. Adsorption isotherm: light circles: Tl^+, Ag^+, Pb^{2+}, Co^{2+}, In^{3+}; dark circles: Na^+, Ca^{2+}, Al^{3+}

Procedure. Through the column, pass 20-30 ml of methylene blue solution, collecting the outgoing liquid in an empty vessel and allowing the excess solution to run off. Silica gel becomes dark blue. Wash the column with water. Put another empty vessel under the column and wash the dark blue silica gel with water from a washer. Collect the outgoing colourless liquid in the vessel (against a white screen).

Experiment 71. Adsorption of Litmus by Aluminium Hydroxide and Barite Powder

The effect of the size and charge of a surface on adsorption may be demonstrated by litmus adsorption on a highly developed surface of aluminium hydroxide in comparison with adsorption on crystal barite powder $BaSO_4$.

Reagents

Litmus, 2 per cent solution.

Aluminium hydroxide, freshly-precipitated.
Barite, powder.
Ammonia, 2 *M* solution.

Procedure. Take three cylinders and in each of them put 5 ml of litmus solution, 300 ml of water and 5 ml of ammonia solution. At the lecture, add freshly-precipitated aluminium hydroxide to one cylinder. Add barite powder to another cylinder, and strongly shake both cylinders. Keep the third cylinder for reference. In the first cylinder, the liquid is almost colourless, and the precipitate becomes dark blue. In the second one, the colour of the solution remains almost unchanged.

Isomorphous Coprecipitation

The solid phase that is separated from a solution may consist of two or more components that are uniformly distributed throughout the crystal volume. In this case, mixed crystals are formed, i.e., cocrystallization or isomorphous coprecipitation occurs. A prerequisite of isomorphous coprecipitation is the equality of charges and the proximity of the ionic radii of macro- and microcomponents. The dimensions of ionic radii should be shown (Fig. VI-10). A very graphic model is that of a crystal lattice, such as sodium chloride, which consists of spherules of different diameters and colour that schematically represent ions. Note that only ions of a similar radius are replaced. In demonstrating ion replacement in a crystal lattice, a set of balls of a different diameter and colour is used (Fig. I-12). The crystals of celestite $SrSO_4$ and anglesite $PbSO_4$, or of strontianite $SrCO_3$ and cerusite $PbCO_3$, may also be shown and it may be noted that these pairs form a similar crystal lattice.

For comparing isomorphous coprecipitation with other types of impurity distribution throughout the precipitate, an illustration may be used to show internal adsorption, such as the adsorption of chloride ions in barium sulphate (Fig. VI-11).

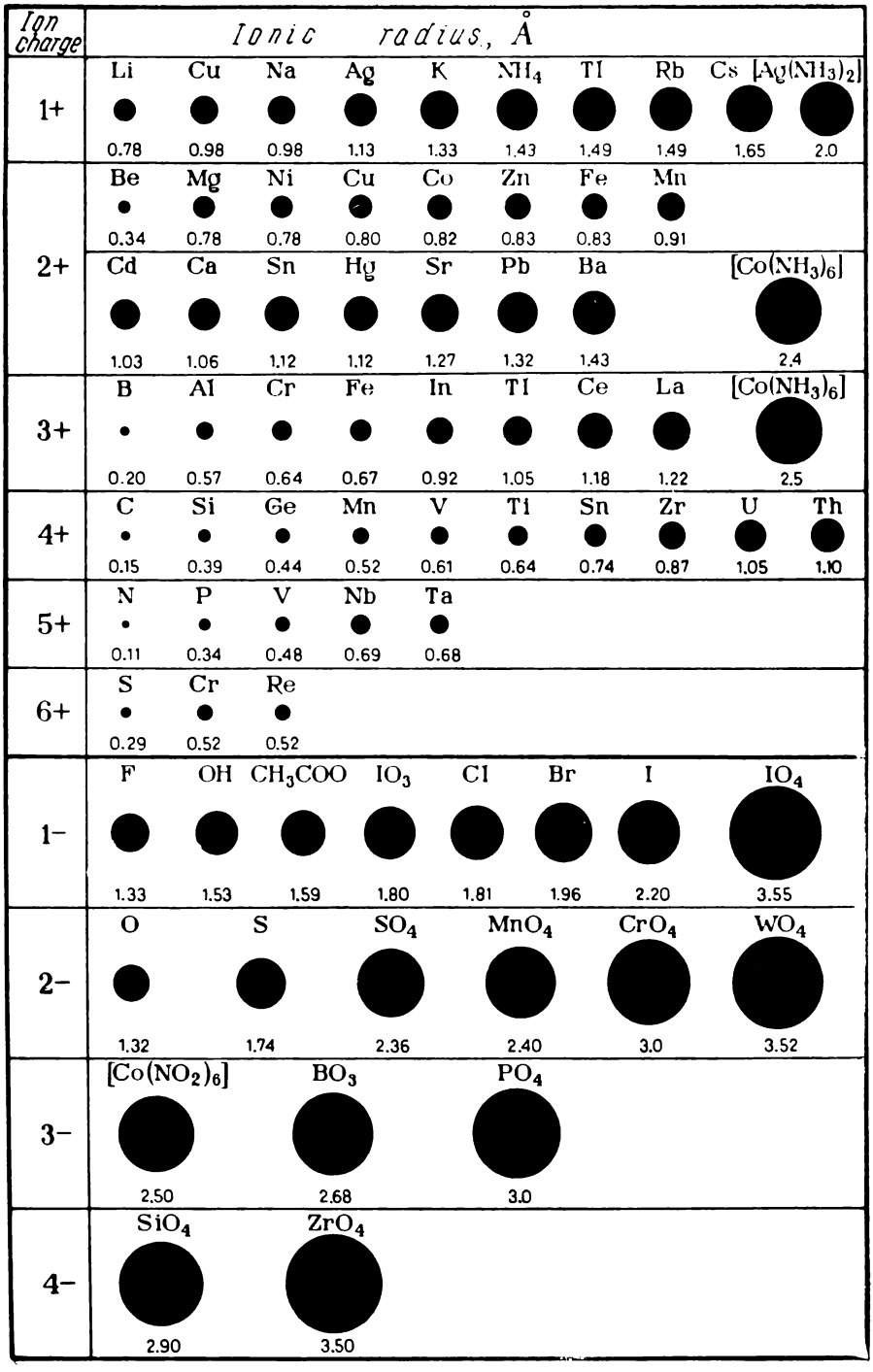


Fig. VI-10. Ionic radii

Experiment 72. Coprecipitation of the Ions of Some Elements with Zinc Mercurotetrathiocyanate

Cobaltous, nickelous, cupric and ferrous ions isomorphously coprecipitate with a precipitate of zinc mercurotetrathiocyanate due to the proximity of their ionic radii with the zinc radius. The replacement of zinc atoms with

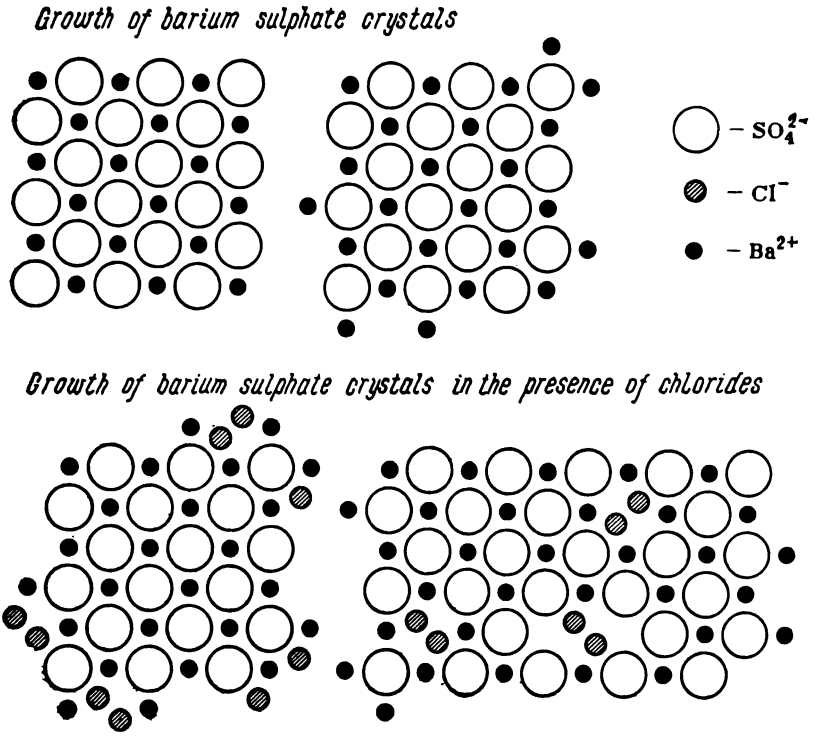


Fig. VI-11. Coprecipitation of chloride ions with barium sulphate

the atoms of other metals leads to a change in the colour of the precipitate due to the deformation of the crystal lattice (Table VI-4). This is illustrated very clearly when copper ions are coprecipitated.

Reagents

Ammonium mercurotetrathiocyanate, 5 per cent solution.

Zinc dichloride, 5 per cent solution.

Cobaltous, cupric, nickelous and ferrous chlorides, 1 per cent solutions.

Table VI-4

IONS THAT ISOMORPHOUSLY COPRECIPITATE WITH ZINC MERCUROTETRATHIOCYANATE

Ion r_i, Å		Compound colour	
		without Zn^{2+}	with Zn^{2+}
Zn^{2+}	0.83		White
Co^{2+}	0.82	Dark blue	Blue
Ni^{2+}	0.78	Pale green	Dirty green
Fe^{2+}	0.83	Yellow	Green
Cu^{2+}	0.80	Yellow-green	Violet
Pb^{2+}	1.32	Is not coprecipitated	

Procedure. In several cylinders, put salt solutions: in one cylinder, put 50 ml of zinc chloride; in another, 10 ml of cobaltous chloride; in the third, 5 ml of cupric chloride, in the fourth, 25 ml of nickelous chloride, and in the fifth, 30 ml of ferrous chloride. Dilute the solutions to 300 ml with water. At the lecture, add 30 ml of ammonium mercurotetrathiocyanate solution to every cylinder. Note that a white precipitate of zinc mercurotetrathiocyanate is formed only in the first cylinder. A precipitate is not formed in the other cylinders. To each of these cylinders, add 20 ml of zinc chloride solution and stir. Coloured precipitates of mixed mecrurotetrathiocyanate of zinc with the metals are slowly formed.

Experiment 73. Coprecipitation of Microquantities of Radioactive Cobalt with Zinc Mercurotetrathiocyanate

The experiment of coprecipitation of radioactive cobalt with zinc mercurotetrathiocyanate is very graphic. In demonstrating the experiment, it is necessary to draw the attention of the audience to the fact that the tracer method makes it possible to keep track of the behaviour of elements when their concentrations are very small, and

that the method is widely used in analytical chemistry and radiochemistry to study coprecipitation [17].

To demonstrate the completeness of coprecipitation, use may be made of the radioactive isotope ^{60}Co, whose half-life is 5.27 years and radiation energy γ is 1.171 MeV and β is 0.306 MeV.

Equipment and Reagents

Computing and recording unit with a reproducer, an audio amplifier and a counter tube.

Stand with test tubes on an enamel tray or a cuvette.

Salt of radioactive cobalt ^{60}Co, a solution with an activity of about 2000 impulses/min·ppm.

Zinc dichloride, 1 per cent solution.

Ammonium mercurotetrathiocyanate, 5 per cent solution.

Procedure. Switch on the computing and recording unit several minutes before the experiment. Draw the attention of the audience to rare light signals or separate clicks due to cosmic rays (background) that are observed on the counter panel. The frequency of the signal should be regulated beforehand; this frequency should not be higher than 10-15 signals per minute. In a test tube with a capacity of 20 ml, put 1 ml of radioactive cobalt salt solution. Bring the test tube to a counter tube, having opened the lid of the lead house. In this case, frequent light and sonic signals are observed; they are due to the γ-radiation of ^{60}Co. On a special tray, carry out an experiment in zinc mercurotetrathiocyanate precipitation. To a test tube with radioactive cobalt salt, add 5 ml of zinc chloride solution and an equal amount of the ammonium mercurotetrathiocyanate solution. Stir with a glass rod and filter the precipitate through a prepared dense filter, collecting the filtrate in an empty test tube. After filtering the bulk of the precipitate, put the funnel with the filter into an empty test tube and bring it to a counter tube. Note that the frequency of sonic and light signals is the same as when the test tube with the radioactive cobalt solution was brought up. It follows that all the cobalt is in the precipitate. Remove the funnel with the test tube and bring the test tube with the filtrate to the counter

tube. Note the absence of radioactive cobalt in the filtrate.

Note. The stand with test tubes and the flask with reagents should be kept on a special enamel tray or a cuvette. The precipitate should be settled and filtered likewise on a tray. Prior to the experiment, the lecture assistant should put on rubber gloves. After the experiment, radioactive precipitates and solutions must not be thrown into common dust bins and poured out into a sink. They should be turned over to special depositories of radioactive isotopes.

The radioactive cobalt salt solution must be kept in a special lead-shielded safe. If the solution accidentally falls on the lecture table or on the floor, the liquid should be collected with a sheet of filter paper and the contaminated place washed with a 10 per cent citric acid solution, and then the absence of radioactive radiation should be checked by a dosimeter [20].

Experiment 74. Coprecipitation of Potassium Permanganate with Barium Sulphate

A special case of isomorphous coprecipitation is the double replacement of ions, when a pair of ions is replaced with another pair of ions that is commensurable with the first pair by its overall dimensions. According to the data obtained by Grim [13], this double replacement may occur if two salts have the same type of crystal structure and form crystals of the same shape with crystal-lattice dimensions that do not differ greatly. The most typical example is coprecipitation of potassium permanganate with a barium sulphate precipitate. The ionic radii are: $K^+ = 1.33$ Å; $Ba^{2+} = 1.43$ Å; $MnO_4^- = 2.40$ Å; $SO_4^{2-} = 2.36$ Å. Other examples of possible substitutions of ion pairs are: $BaCrO_4$ and $KMnO_4$, $BaSeO_4$ and $KMnO_4$.

Reagents

Potassium permanganate, 1 per cent solution.
Sulphuric acid, 9 *M* solution.
Barium chloride, 20 per cent solution.
Sodium sulphite, 1 per cent solution.

Procedure. In a cylinder, put 10 ml of potassium permanganate solution, 100 ml of water and 20 ml of sulphuric acid solution. In another cylinder, put 100 ml of water and 20 ml of sulphuric acid solution. At the lecture, add 20 ml of barium chloride solution to each cylinder while vigorously stirring. Barium sulphate precipitates are formed in both cylinders. To the second cylinder, add 10 ml of potassium permanganate solution and stir. Then, add sodium sulphite solution to both cylinders until the potassium permanganate solution is decoloured. Draw the attention of the audience to the fact that in the first cylinder, where potassium permanganate coprecipitated isomorphously, the barium sulphate precipitate has a pink colour. In the second cylinder, where potassium permanganate was able to adsorb on the surface, the barium sulphate precipitate has a pink colour. In the second cylinder, where potassium permanganate was able to adsorb on the surface, the barium sulphate precipitate is white.

Experiment 75. Coprecipitation of the Cupric Ion With Cadmium Ferrocyanide

For concentrating copper traces, use may be made of the coprecipitation of copper ions with cadmium ferrocyanide. The replacement of cadmium ions with copper ions in the crystal lattice of cadmium ferrocyanide leads to a change in the colour of the precipitate from white to crimson [21].

Reagents
Cadmium chloride, 1 per cent solution.
Cupric sulphate, 0.1 per cent solution.
Potassium ferrocyanide, 10 per cent solution.
Ammonia, 2 *M* solution.

Procedure. In one cylinder, put 20 ml of cadmium chloride solution and 130 ml of water, and in another, 8 ml of copper sulphate solution and 150 ml of water. At the lecture, add to each cylinder 100 ml of ammonia solution and 20 ml of potassium ferrocyanide solution. A white precipitate is formed in the cylinder with cadmium chloride, and no precipitate is formed in the cylinder with

copper sulphate traces. To the cylinder with copper sulphate, add 20 ml of cadmium chloride solution and vigorously stir. The formation of a crimson precipitate of a mixed complex having the composition of $(Cu, Cd)_2[Fe(CN)_6]$ is observed.

PRECIPITATION TITRATION

Many precipitation reactions that proceed quite rapidly and stoichiometrically are successfully used in titrimetric analysis. In expounding the method of precipitation titration, it is necessary to show the curves of titration of

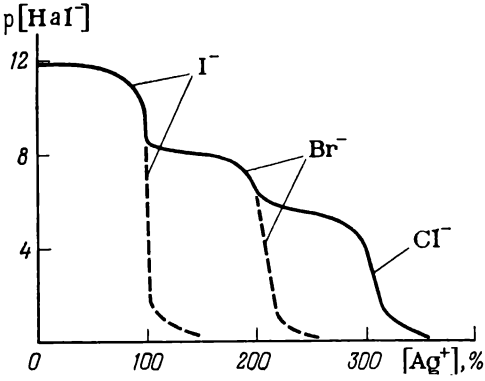


Fig. VI-12. Curves of titration of 0.01 *M* halide solutions by silver nitrate. Continuous line: rated curve for mixtures; dotted line: rated curves for iodide and bromide, respectively

halide ions by silver ions, emphasizing the dependence of the titration jump on the solubility product of silver halide (Fig. VI-12).

For determining the end point of titration, use is made of different indicators, particularly adsorption indicators. Substances that reversibly change their colour on the surface of a precipitate that is formed during titration are usually called adsorption indicators. The ions of the indicator, which is an acid or base dye, replace ions of the same sign of the outer double layer of particles. A colour

change occurs due to the strong deformation of a dye ion under the action of the adsorbed ions of the precipitate.

Adsorption is an indispensable but insufficient condition for indicating the equivalence point by means of adsorption indicators. A change in such physicochemical constants of adsorbed dyes as the solubility product, the oxidation-reduction potential and the ionization constant is important for indication. A change in one of these constants is decisive for the indicator colour change at the titration end point [22, 23].

Experiment 76. Titration of Sodium Chloride by Silver Nitrate in the Presence of Fluorescein as Adsorption Indicator

The colloidal particles of silver chloride are overcharged in the process of titration of a chloride ions by silver ions. The positively charged colloidal particles $AgCl \cdot Ag^+ \vdots NO_3^-$ are formed beyond the equivalence point. The anion of the fluorescein indicator (L) is adsorbed on a positively charged surface, participating in the reaction:

$$AgCl \cdot Ag^+ \vdots NO_3^- + HL \rightleftarrows AgCl \cdot Ag^+ \vdots L^- + NO_3^- + H^+$$

Due to the deformation of the fluorescein anion, the colour of the adsorbed indicator changes from yellow-green to pink [21].

Reagents

Silver nitrate, 0.1 *N* solution (keep in a dark flask).
Sodium chloride, 0.1 *N* solution.
Fluorescein, 0.1 per cent ethanol solution.

Procedure. In a conical 500-ml flask, put 5 ml of sodium chloride solution and 200 ml of water. At the lecture, add 50 drops of fluorescein solution. Slowly add silver nitrate solution while stirring until the colour changes from yellow-green to pink.

Experiment 77. Titration of Lead Nitrate by Potassium Chromate in the Presence of Congo Red as Adsorption Indicator

The anion of the indicator of congo red is adsorbed, and the colour changes from red to dark green, on the positively-charged colloidal particles $PbCrO_4 \cdot Pb^{2+} \vdots NO_3^-$, which

are formed beyond the equivalence point when chromate ions are titrated by lead ions:

$$PbCrO_4 \cdot Pb^{2+} \vdots NO_3^- + L^{2-} \rightleftarrows PbCrO_4 \cdot Pb^{2+} \vdots L^{2-} + NO_3^-$$

According to Schulek, the adsorption effect is accompanied with the acceptance and loss of hydrogen ions. Hence, a colour change is due to the acid-base properties of the indicator [23]:

$[PbCrO_4]CrO_4H^- + OH^-$ = before the equivalence point (the colour of congo red is red)

$[PbCrO_4]Pb^{2+} + H^+$ = beyond the equivalence point (the colour of congo red is dark blue)

Reagents

Lead nitrate, 0.1 *N* solution.

Potassium chromate, 0.1 *N* solution.

Congo red, 0.1 per cent solution.

Procedure. In a conical flask, put 5 ml of potassium chromate solution and 200 ml of water, and add 3 ml of indicator solution. Slowly titrate with a lead nitrate solution. An orange colloidal solution of lead chromate appears. At the equivalence point, the colour of the precipitate sharply changes to dark green.

Experiment 78. Titration of Sodium Chloride by Silver Nitrate in the Presence of Rhodamine 6 G as Fluorescent Adsorption Indicator

Some organic substances that fluoresce in a solution may lose their power to fluoresce when adsorbed [24]. For example, when a silver nitrate solution is titrated by a sodium chloride solution in the presence of rhodamine 6 G, yellow-green fluorescence vanishes at the equivalence point, since the cation of the (R^+)-indicator is adsorbed by the negatively charged surface of the precipitate:

$$AgCl \cdot Cl^- \vdots Na^+ + R^+ \rightleftarrows AgCl \cdot Cl^- \vdots R^+ + Na^+$$

Reagents

Equipment

Instrument for titration with fluorescent indicators (see Fig. V-3).

Sodium chloride, 0.1 *N* solution.
Silver nitrate, 0.1 *N* solution.
Rhodamine 6 G, 0.1 per cent solution.

Procedure. In a conical 300-ml flask, put 5 ml of silver nitrate solution and 100 ml of water. At the lecture, add 1 ml of rhodamine 6 G solution. Switch off the light and put the flask in the path of an ultraviolet flux. The solution has a yellow fluorescence. Titrate with the sodium chloride solution from a burette until fluorescence disappears.

Note. Similar experiments may be demonstrated by using fluorescein in titrating sodium chloride by silver nitrate (extinction of fluorescence), or silver nitrate by sodium chloride (appearance of fluorescence), and also eosin and other indicators.

Experiment 79. Titration by Mohr's Method

Silver chloride and silver chromate have different solubility ($S_{AgCl} = 1.3 \cdot 10^{-5} M$, $S_{Ag_2CrO_4} = 0.7 \times 10^{-4} M$). Therefore, in titrating chloride ions in the presence of chromate ions that serve as an indicator, first a white precipitate of silver chloride is formed, and brick red silver chromate precipitates near the equivalence point.

Reagents
Silver nitrate, 0.1 *N* solution.
Sodium chloride, 0.1 *N* solution.
Potassium chromate, 5 per cent solution.

Procedure. In a conical flask, put 5 ml of sodium chloride solution, 200 ml of water and 25 drops of indicator. Titrate with the silver nitrate solution until a red precipitate appears.

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CHAPTER VII

Colloidal systems

Colloidal systems contain particles with a diameter of 10^{-7}-10^{-4} cm. The stability of the colloidal disperse systems is due to the electric repulsion of charged particles. The particle charge is caused by the adsorption of common ions or other potential-determining ions by the surface of a solid phase. The difference of potentials between a solid substance and a solution may be expressed by the equation

$$\Delta E = \frac{RT}{zF} \Delta \ln c$$

where z = charge of the potential-determining ion;
c = its concentration.

The counter-ions from a solution that are retained at the charged surface owing to electric attraction create a double electric layer [1-3]. It is expedient to show diagrams of a colloidal particle (Fig. VII-1) and of a double electric layer (Fig. VII-2) to the audience.

Colloidal systems are usually subdivided into lyophobic and lyophilic ones. Lyophobic colloidal systems are disperse systems in which the dispersed phase irreversibly interacts with the dispersion medium (coagulation). They are characterized by relatively high sensitivity to the coagulating action of electrolytes. The dispersed phase of lyophilic colloidal systems reversibly interacts with the dispersion medium, i.e., it is peptized. Lyophilic colloidal systems are poorly sensitive to electrolytes and are comparatively viscous.

In chemical analysis, the formation of colloidal systems is a negative phenomenon; however, in some cases, colloid formation is used in analysis, for example, in nephelometry.

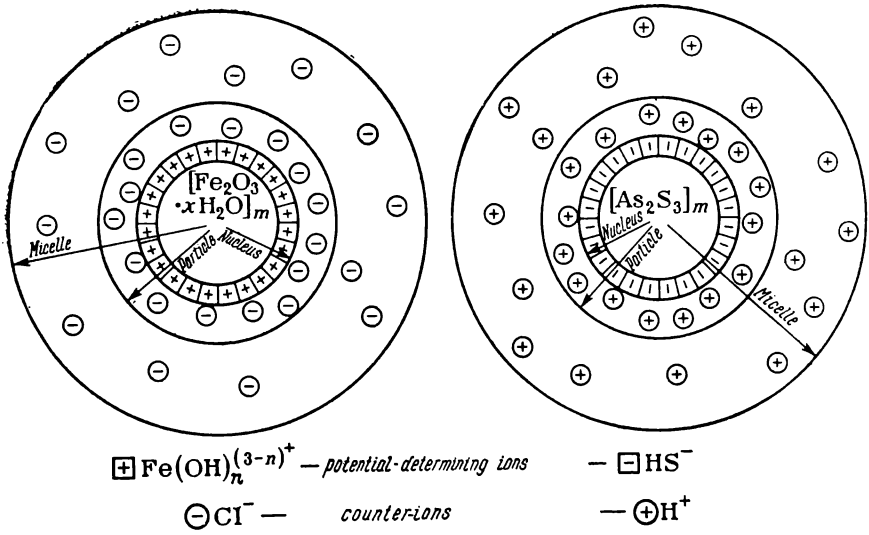

Fig. VII-1. Diagrams of the micelles of iron hydroxide and arsenic sulphide

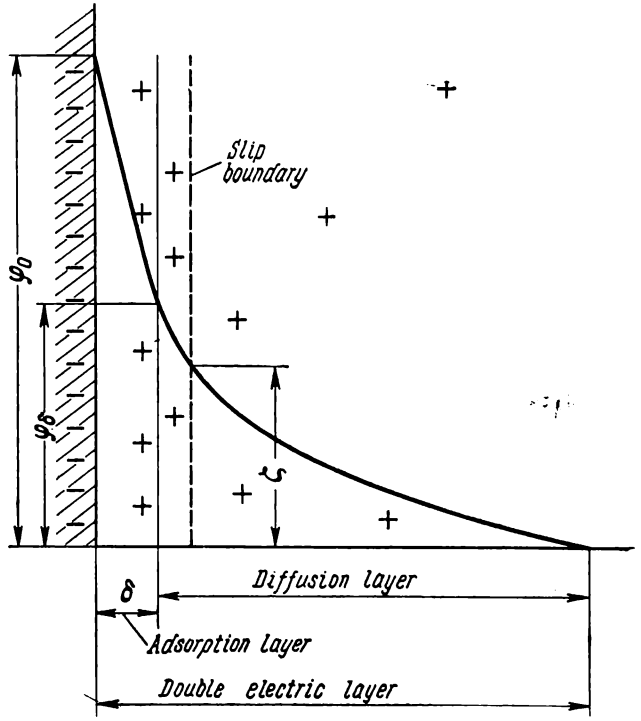

Fig. VII-2. Structure of a double electric layer

PREPARATION OF COLLOIDAL SYSTEMS

Substances in a colloidal state may be prepared by two methods: crushing coarse particles (dispersion method) and forming aggregates from separate molecules (condensation method). The second method is usually used in practice; it is based on different chemical reactions (hydrolysis, oxidation-reduction, and so forth). By regulating the conditions of a process, it is possible to separate substances in the form of colloidal particles of different degree of dispersion.

Different colloidal systems may be prepared right at a lecture, but to save lecture time it is better to prepare them beforehand and put them on the demonstration table with the appropriate labels. Practically all substances may be produced in a colloidal state. The methods of preparing some of them are given below.

Experiment 80. Preparation of the Sulphur Sol from Its Saturated Ethanol Solution

Sulphur forms a lyophobic colloidal system with negatively charged particles.

Reagent

Sulphur, saturated solution in anhydrous ethanol. It is prepared by long standing, and the undissolved part of sulphur is filtered off [4].

Procedure. The sulphur ethanol solution is poured dropwise into a beaker filled with distilled water while stirring. A milk-white opalescent sol of sulphur is formed. Observe the experiment against a black screen.

Experiment 81. Preparation of the Sulphur Sol from Sodium Thiosulphate

Sodium thiosulphate in an acid medium slowly decomposes with the separation of sulphur in a finely-dispersed state. The stability of the colloidal system depends on the initial quantities of thiosulphate and acid:

$$S_2O_3^{2-} + 2H^+ = S\downarrow + SO_2\uparrow + H_2O$$

Reagents

Sodium thiosulphate, 1 per cent solution.
Hydrochloric acid, 2 *M* solution.

Procedure. In a cylinder, put 5 ml of sodium thiosulphate solution, 400 ml of water and 5 ml of hydrochloric acid. A white sol of colloidal sulphur slowly appears.

Note. A sulphur sol prepared by the given method is unstable; therefore, it should be prepared immediately before a lecture. The formation of the sulphur sol may be demonstrated at the lecture; in this case, the concentration of solutions should be increased.

Experiment 82. Preparation of the Gel of Silicic Acid

Silicic acid forms a lyophobic negatively-charged gel; freshly-precipitated silicic acid exhibits properties of a lyophilic colloidal system [5]:

$$[(SiO_2 \cdot pH_2O)_m \cdot nHSiO_3^- \cdot (n-x)\,H^+]^{x-} \cdot xH^+$$

It should be noted that a considerable part of silicic acid may be in a colloidal state in a solution. This is used in express analysis during the precipitation of elements without the preliminary separation of silicon.

It is necessary to show a diagram of the state of silicic acid in conformity with the solution acidity (Fig. VII-3) [6].

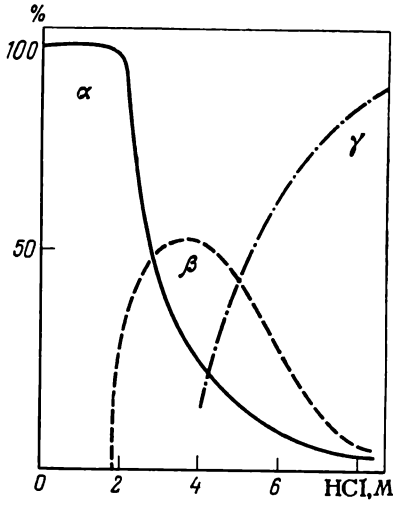

Fig. VII-3. Diagram of the state of silicic acid (*a*, β, γ) in a hydrochloric acid solution

Reagents

Sodium silicate, 10 per cent solution.
Hydrochloric acid, concentrated.

Procedure. Pour 200 ml of sodium silicate solution beforehand into a cylinder or a beaker. At the lecture, add 10 ml of hydrochloric acid while vigorously stirring with

a glass rod, which should be kept vertically in the beaker. Soon, faint opalescence appears; gradually it becomes more pronounced, and the contents of the beaker solidify. The rod remains in a vertical position [4].

Experiment 83. Preparation of the Sol of Ferric Hydroxide

When iron (III) salts are hydrolyzed, the sol of iron hydroxide with positively-charged particles is formed:

$$[(Fe_2O_3 \cdot pH_2O)_m \cdot nFe(OH)_2^+ \cdot (n - x)\,Cl^-]^{x+} \cdot xCl^-$$

Reagent

Ferric chloride.

Procedure. In a 1-litre beaker, put 800 ml of water, heat almost to boiling, add about one gram of ferric chloride on the tip of a glass spatula and stir. A transparent sol of red colour is formed.

Experiment 84. Preparation of the Sol of Arsenous Sulphide

The colour of the sol of arsenic trisulphide changes from yellow to orange, depending on the concentration. An orange sol solution may contain up to 5 moles of arsenic sulphide per litre, while its solubility is about 10^{-7} moles.

Reagents

Arsenous acid, saturated solution. Three grams of arsenous anhydride are dissolved in 500 ml of water while boiling.

Hydrogen sulphide, gas.

Procedure. Pour 50 ml of water into a 300-ml flask. Slowly pass hydrogen sulphide through, simultaneously adding 150 ml of arsenous acid solution dropwise. A yellow opalescent sol of arsenic sulphide is formed [7].

Experiment 85. Preparation of the Gold Sol

Gold in a colloidal state is prepared by reducing gold salts. Depending on the degree of dispersion, sol colour changes from the blue of a coarse-dispersed sol (Fig. VII-4) [8] to the red of a fine-dispersed sol.

Preparation of the Blue Sol

Reagents

Chloroauric acid, 0.1 per cent solution.

Hydrazine hydrochloride, 0.1 per cent solution.

Procedure. To 400 ml of water, add 30 ml of chloroauric acid solution and 20 ml of hydrazine hydrochloride solution. A transparent blue sol of gold is formed.

Preparation of the Red Sol

Reagents

Chloroauric acid, 0.1 per cent solution.

Potassium carbonate, 1 per cent solution.

Tannin, 1 per cent solution.

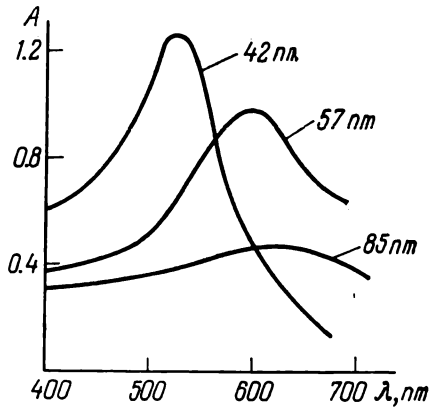

Fig. VII-4. Light-absorption spectra of gold sols in the case of different degrees of dispersion (particle dimensions are indicated on the curves)

Procedure. In a beaker, put 400 ml of water, 10 ml of chloroauric acid solution and 2 ml of potassium carbonate solution. Add a tannin solution (desirably on heating) dropwise while stirring. A red transparent sol is formed.

Experiment 86. Preparation of the Gel of Calcium Carbonate

As we have seen, many substances may be prepared in a colloidal state, even such substances as calcium carbonate, if the precipitation reaction is carried out under specially selected conditions [9].

Reagents

Calcium chloride, 4 *M* solution. 44 g of anhydrous salt are dissolved in hot water, filtered and diluted to 100 ml with water.

Sodium carbonate, 2 *M* solution.

Procedure. Put 10-12 ml of calcium chloride solution in a test tube or a cylinder with a capacity of 50 ml. By a pipette, collect 20-25 ml of sodium carbonate solution. Lower the pipette tip to the bottom of the vessel, slowly discharge the solution and at the same time carefully raise the pipette. A transparent gel of calcium carbonate is formed (turn over the test tube!). If a gel is not formed, shake the test tube. The solution solidifies into a white opaque jelly. Carefully turn over the test tube, showing that its contents have solidified. In 20-30 minutes, the existence of the gel ends. A white loose precipitate of calcium carbonate appears on the bottom of the test tube. The precipitation of calcium carbonate may be effected at the same time, diluting the afore-mentioned quantities of the reagents to double their amount with water and heating them to the boiling point in different beakers. After mixing the hot solutions together, calcium carbonate rapidly settles to the bottom in the form of an ordinary precipitate.

PROPERTIES OF COLLOIDAL SYSTEMS

Size and Charge of Colloidal Particles

Experiment 87. Tyndall Effect

If a strong flux of light rays is passed through a colloidal system, a light cone (the Tyndall cone) is observed in the colloidal system as a result of light scattering by colloidal particles; this cone is well seen in the dark. Under these conditions, the true solution appears to be "optically void".

It should be noted that such a method is used to prove the absence of colloidal particles in solutions. The Tyndall effect is employed also in nephelometric analysis.

Equipment and Reagents

An instrument for demonstrating the Tyndall effect (see Fig. I-5).

Silver nitrate, 1 per cent solution.

Procedure. Take three tall 1-litre beakers and put beforehand: 700 ml of distilled water into one beaker, 600 ml

of distilled water and 100 ml of tap water into another beaker, and 300 ml of distilled water and 400 ml of tap water into the third beaker. Add 10 ml of silver nitrate solution to each beaker. Put the three beakers on a sheet of black paper. In an ordinary light, no difference is observed between the first and second beakers; a white opalescent sol of silver chloride is observed in the third beaker. Darken the auditorium. Put the beakers alternately on the table of the instrument, observing the Tyndall cone in the second and third beakers. The cone will be absent in the first beaker if the water is sufficiently distilled.

Note. Since the content of chloride ions may be different in tap water, the ratio of the volumes of tap water and distilled water should be selected beforehand so that the opalescence of silver chloride might not be observed visually in the second beaker, but at the same time the Tyndall cone might be sufficiently clear.

Experiment 88. Charge of Colloidal Particles

The particles of colloidal systems have an electric charge due to the selective adsorption of ions of a certain sign from a dispersion medium. The charge sign of a colloidal particle may be determined by the direction in which particles move in an electric field (electrophoresis). But electrophoresis is too long for lecture demonstrations. At the lecture, it is more convenient to show the different migration of colloidal particles on a charged surface. The migration potential (like the velocity of particles in an electric field) is determined by the value of the electrokinetic potential (the electric potential at the boundary between a water layer that is strongly bound with a particle and the entire mass of the solution). As a charge surface, use may be made of chromatographic paper, which is charged negatively in water; therefore, only particles with a negative charge can move through the paper.

The experiment of determining the particle charge may be shown most conveniently by using coloured organic substances (dyes) [10]. The ions of acid dyes (fluorescein, eosin) carry a negative charge and easily move through

the paper, while the ions of base dyes scarcely move at all (rhodamine 6 *G*, methylene blue).

Equipment and Reagents

Cylinders with caps, to which hooks are attached (Fig. VII-5).
Eosin, 0.5 per cent sodium salt solution.
Methylene blue, 0.01 per cent solution.
Chromatographic paper.

Procedure. In one cylinder, put 30 ml of eosin solution, and in the other, 20 ml of methylene blue solution. Attach strips of filter paper to the cylinder caps by hooks and lower them into the dye solutions. Several minutes later, draw the attention of the audience to the fact that eosin has risen up along the paper, while methylene blue remained at the starting line.

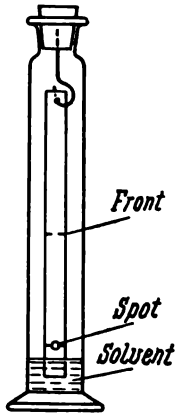

Fig. VII-5. Chamber for producing a one-dimensional anabatic chromatogram

Experiment 89. Repeptization of a Cobalt Sulphide Precipitate on Washing

When the precipitates are washed with water, the coagulated particles reassume their initial electrokinetic potential and become dispersed. Strong dilution with water is not always accompanied with repeptization, since factors promoting the perfection of the precipitate surface (recrystallization) act simultaneously.

Reagent

Cobalt sulphide, freshly precipitated.

Procedure. Immediately before the lecture, produce a cobalt sulphide precipitate by passing hydrogen sulphide through a cobalt salt solution in an ammonia medium in the cold. Filter the precipitate. At the lecture, wash the precipitate on a filter with water, putting a cylinder with water under the funnel with the filter. The appearance of a dark turbid solution is observed as the precipitate is washed.

Stability of Colloidal Systems

The stability of colloidal systems is connected with the surface charge (primary stability) and with the effect of repulsion of colloidal particles (secondary stability). Primary stability is determined by the total potential of the particles of a solid substance, and secondary stability, mainly by the electrokinetic potential. Lyophilic colloidal systems are more stable than lyophobic ones.

Experiment 90. Coagulation of the Colloidal System of Ferric Hydroxide

The agglutination of colloidal particles and the formation of more complex aggregates from them is known as coagulation. Inorganic colloidal systems especially tend to coagulate under the action of high-charge electrolytes. The effect of different electrolytes on coagulation is compared by using the value of the coagulation threshold (minimum electrolyte concentration that causes coagulation). It is expedient to present a table of the values of coagulation thresholds for different sols (Table) [3].

Table

MEAN VALUES OF COAGULATION THRESHOLDS FOR DIFFERENT SOLS (MMOL/L)

Sols	Counter-ions			
	singly-charged	doubly-charged	three-charged	four-charged
Negatively charged				
arsenic sulphide	55	0.69	0.091	0.090
gold	24	0.38	0.006	0.0009
silver iodide	142	2.43	0.068	0.013
Positively charged				
iron hydroxide	11.8	0.21	—	—
aluminium hydroxide	52	0.63	0.080	0.053

Reagents

Sol of ferric hydroxide (see sol preparation in Experiment 83).

Sodium sulphate, saturated solution.
Sodium hydroxide, 2 *M* solution.

Procedure. At the lecture, pour the sol of iron hydroxide into two cylinders. Keep one cylinder for reference. To the other cylinder, add 50 ml of sodium sulphate solution or alkaline solution. Coarse red-brown flakes are formed, and they settle out to the bottom of the cylinder. The solution above the precipitate becomes colourless.

Note. An excess of a coagulator should not be used in order to avoid the overcharging of colloidal particles.

Experiment 91. Stabilization of the Colloidal System of Antimony Sulphide by Gelatin

When lyophilic colloidal systems (for example, gelatin) are added to lyophobic colloidal systems, the former are adsorbed on the surface of lyophobic particles, forming the so-called "protective layer". By electrokinetic properties, such a system is lyophilic, and this reduces the power of a lyophobic sol to coagulate.

Reagents
Antimonous chloride, 1 per cent solution in 2 *N* hydrochloric acid solution.
Gelatin, 1 per cent solution. One gram of gelatin is dissolved in 100 g of water while heating and stirring.
Hydrogen sulphide, saturated solution.

Procedure. In a cylinder, put 25 ml of antimony chloride solution, 40 ml of concentrated hydrochloric acid and 400 ml of water. At the lecture, divide the solution into two parts. To one part, add hydrogen sulphide water; an orange precipitate of antimony sulphide is formed. To the other part, add 100 ml of gelatin solution and hydrogen-sulphide water; a yellow transparent sol of antimony sulphide is formed.

Adsorption

To explain the properties of colloidal systems, it is necessary to take account of the presence of interface, which makes it possible for the most diverse adsorption phenomena to occur. Adsorption is the concentration of substan-

ces at the interface as a result of molecular and electrostatic interaction. Wetting phenomena are close to adsorption phenomena; the former are likewise determined by the intensity of interaction between molecules of different substances. Adsorption from a solution is of great importance to most physicochemical processes.

According to the polarity equalization rule formulated by P. A. Rebinder [2], a substance may be adsorbed at the interface if the difference in the polarities of the phases is equalized. It follows that diphilic molecules of a substance that have an asymmetric structure and contain hydrophilic (polar) and hydrophobic (non-polar) groups, and that are in the surface layer, are oriented in a way that by their polar part they are turned to the polar phase, and by their non-polar part, to the non-polar phase. Therefore, the metal chelates that have a large hydrophobic surface and that are poorly wetted with water (8-hydroxyquinolinates, dimethylglyoximates, etc.) concentrate in the form of a film at the liquid-liquid interface in the case of extraction (flotation effect) and the creepage of precipitate particles along the glass walls on filtration [11].

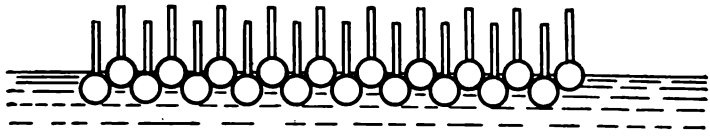

Fig. VII-6. Monomolecular layer of a surfactant on a liquid surface. "Langmuir's palisade"

The role of polar groups is played by $-NH_2$, —OH, —COOH, etc., and the role of non-polar groups is played by hydrocarbon chains or cycles. The molecular arrangement in the surface layer is illustrated in Fig. VII-6.

For the experiment in the flotation of nickel dimethylglyoximate, see Chapter II, Experiment 9.

Experiment 92. Flotation of the Complex of Aluminium with Aluminon

Aluminon (ammonium salt of aurin tricarboxylic acid) forms with the aluminium ion the chelate "lacquer" of red colour.

The flotational extraction of the chelate makes it possible to sharply increase the selectivity of the reaction. Hence, 0.05-0.1 mg of aluminium may be detected in the presence of a 1,500-fold excess of the ions of cobalt, zinc, nickel, manganese and chromium [12].

Reagents

Aluminium trichloride, 0.1 per cent solution.
Aluminon, saturated solution.
Buffer solution (pH = 4.5—5.5). 7.8 g of ammonium acetate, 5.4 g of ammonium chloride and 6 ml of hydrochloric acid (1 : 1) are dissolved in 100 ml of water.
Chloroform.

Procedure. In a cylinder, put 5 ml of aluminium chloride solution, 100 ml of buffer solution and 100 ml of water. At the lecture, add 5 ml of aluminon solution. Lacquer of red colour is formed. Add 100 ml of chloroform. After shaking, a dense red film is formed at the interface.

Note. When the aluminium concentration is larger, a red suspension or flakes are formed in the chloroform layer.

Experiment 93. Wettability of the Surface of Different Substances

Water wets glassware well; therefore, the creepage of high-dispersed precipitates is observed along the walls of a vessel. Such a phenomenon is observed also in respect to saturated salt solutions. To prevent this phenomenon, the walls of vessels are covered with a thin layer of a hydrophobizing substance, such as trichlorosilane. The hydrophobization of the surfaces of beakers, burettes and pipettes is widely practised in ultramicroanalysis. Hydrophobic properties are possessed also by articles made of fluoroplastic-4 and other polymers [13].

For demonstrating the properties of hydrophobic and hydrophilic surfaces, use may be made of the properties of the oriented layer of molecules of stearic acid. When solidifying on the water surface, stearic acid forms an oriented monomolecular layer. The polar groups of stearic acid are turned towards water, and the hydrocarbon residues are turned towards the inside of the stearic layer; this leads

to a change in surface wettability [14]. The change in wettability may be easily observed by using water coloured with methyl violet or other dyes.

Reagents
Stearic acid.
Methyl violet, 0.1 per cent solution.

Procedure. In a 0.5-litre beaker, put 400 ml of water and a piece of stearic acid. At the lecture, heat the beaker. In this case, stearic acid melts. Cool the beaker. Carefully remove the solid layer that is formed, put it on a sheet of filter paper on the table, and dry it. Divide the layer into two pieces. Put one piece so that the oriented layer is upward (i.e., the side which was turned towards water is upward), and put the other piece so that the oriented layer is downward. Put a drop of methyl violet on both pieces. On the surface with the oriented layer, the drop runs, while on the surface of the other piece, it does not run.

Note. In a large auditorium, the experiment (i.e., the application of drops) should be demonstrated with the aid of an epidiascope.

UTILIZATION OF COLLOID FORMATION IN CHEMICAL ANALYSIS

Experiment 94. Detection of Antimony (V) with Rhodamine B

The ion $[SbCl_6]^-$ forms water-insoluble ion pairs with large cations of bases (rhodamine B, methyl violet, brilliant green). A colloidal system is formed when the antimonic ion content is small. For quantitative determinations in a photometric variant, use is made of the stabilization of the colloidal system by gelatin. The reaction is sensitive. The minimum of detection is 10 ppm.

Reagents
Antimonic chloride, 0.5 per cent solution in 6 *M* hydrochloric acid solution.
Rhodamine B, 0.001 per cent solution in 1 *M* hydrochloric acid solution.

Procedure. In a cylinder, put 300 ml of the dye solution. At the lecture, divide the solution into two parts. To one part, add 10 ml of antimony chloride solution and vigorously stir. In the presence of antimony, the light-red glowing solution of the dye becomes violet.

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CHAPTER VIII

Oxidation-reduction reactions

Oxidation-reduction reactions are widely used in analytical chemistry for ion detection (see Experiments 4, 5, 18, 29) and for the electrolytic separation of elements and quantitative determination, especially in titrimetric analysis (see Experiments 11, 56) [1-4].

DIRECTION OF OXIDATION-REDUCTION REACTIONS

The direction and completeness of an oxidation-reduction (redox) reaction is determined by the equilibrium constant

$$\log K = \frac{(E_1^\circ - E_2^\circ) \cdot n}{0.059} \text{ (at 25° C)}$$

where E_1°, E_2° = standard redox potentials of reduction and oxidation half-reactions;
n = number of electrons.

The equilibrium potential (E) is connected with the standard redox potential in the following way (Nernst equation):

$$E = E^\circ + \frac{RT}{nF} \ln \frac{a_{Ox}}{a_{Red}}$$

where a_{Ox} and a_{Red} = activities of oxidized and reduced forms.

On complexation with the participation of the oxidized or reduced form

$$E^\circ_{Ox,\, L/Red,\, L'} = E^\circ_{Ox/Red} \pm \frac{RT}{nF} \ln \beta$$

In the case of the formation of slightly soluble compounds

$$E^{\circ}_{\text{Ox, A/Red. A'}} = E^{\circ}_{\text{Ox/Red}} \pm \frac{RT}{nF} \ln K_{sp}$$

If these activities are replaced by the equilibrium concentrations of potential-determining ions ($a_{\text{Ox}} = f[\text{Ox}]$ or $a_{\text{Red}} = f[\text{Red}]$), we obtain:

$$E = E^{\circ} + \frac{RT}{nF} \ln \frac{[\text{Ox}] \cdot f_{\text{Ox}}}{[\text{Red}] \cdot f_{\text{Red}}} = E^{\circ} + \frac{RT}{nF} \ln \frac{f_{\text{Ox}}}{f_{\text{Red}}} + \frac{RT}{nF} \ln \frac{[\text{Ox}]}{[\text{Red}]}$$

The sum of the first two terms in the right-hand part of the equation corresponds to the formal potential E^{f} of the half-reaction

$$E^{\text{f}} = E^{\circ} + \frac{RT}{nF} \ln \frac{f_{\text{Ox}}}{f_{\text{Red}}}$$

It follows that the formal potential changes in conformity with the ionic strength of the solution.

For a complex system, a change in potential is connected with the effect of various factors (ionic strength of the solution, complex formation, dissociation, association, hydration, etc.):

$$a\text{Ox} + b\text{B} + \ldots + n\bar{e} \rightleftarrows m\,\text{Red} + n\text{A}$$

where B, A = ligands, including H^+ and OH^-.

The potential for such a system is:

$$E = E^{\text{f}} + \frac{RT}{nF} \ln \frac{c^{\text{a}}_{\text{Ox}}}{c^{\text{m}}_{\text{Red}}}$$

where c_{Ox} and c_{Red} = total concentrations of the oxidizing agent and the reducing agent in a solution in all their forms.

E^{f} depends on the concentration of a ligand, H^+, the ionic strength, and so forth.

For analytical purposes, it is the formal potentials that are important, as they make it possible to foresee the direction of chemical reactions in a solution; their value may be determined directly by experiment.

Reactions which occur stepwise with the formation of intermediate products, and especially electrochemical reactions, being incompletely reversible, are characterized by a mixed potential [1, 2].

The standard potentials of pairs are measured relative to the potentials of reference electrodes, such as a stand-

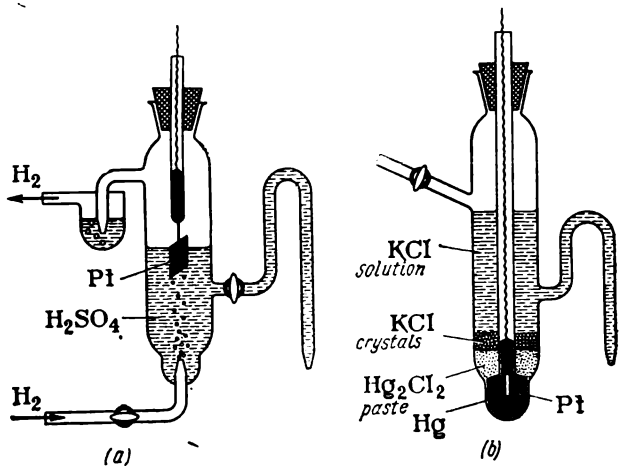


Fig. VIII-1. Reference electrodes:
(a) hydrogen electrode; (b) calomel electrode

ard hydrogen electrode or a calomel half-cell. At the lecture, illustrations of reference electrodes may be shown (Fig. VIII-1). A potentiometric unit for measuring potentials should be put on the demonstration table, and a graphic diagram with the values of standard potentials of some oxidation-reduction pairs should be presented (Fig. VIII-2) [3].

Direction of Reactions in Conformity with the Values of Standard Potentials of Oxidizing and Reducing Agents

Experiment 95. Oxidation-Reduction Properties of the Nitrite Ion

Substances whose standard potential is higher than the standard potential of the system NO_3^-, H^+/HNO_2 (E° = = 0.94 V) oxidize the nitrite ion, for example, the perman-

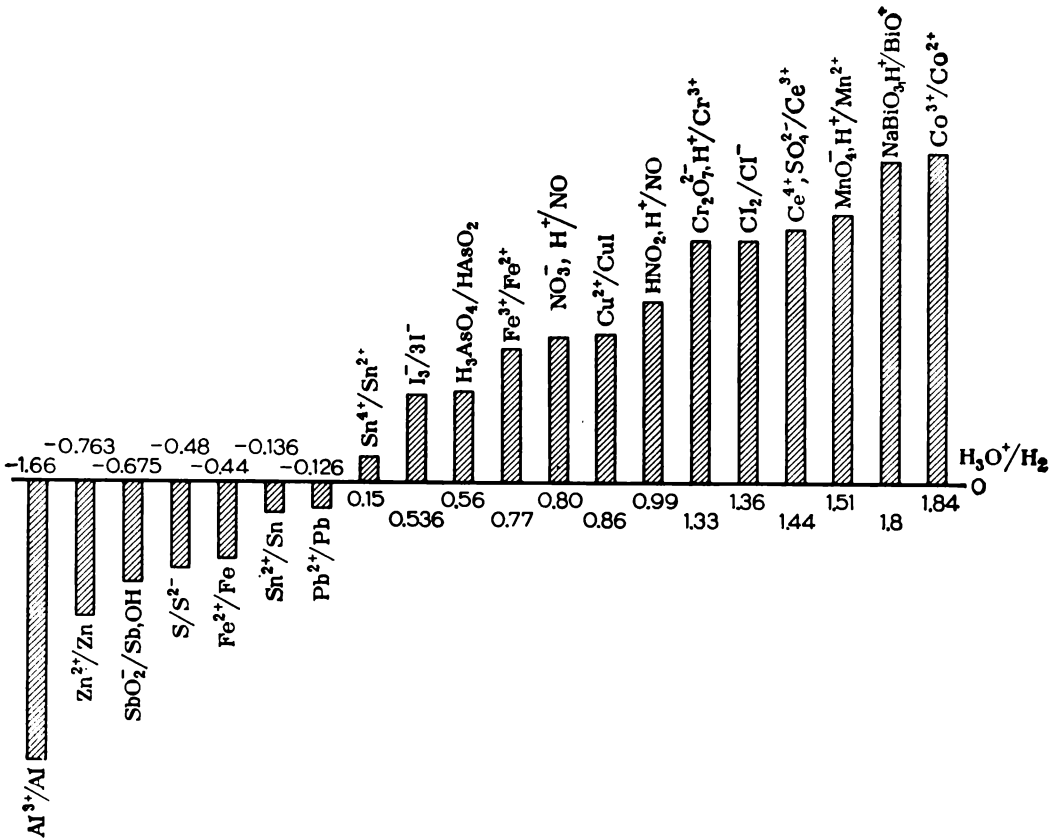


Fig. VIII-2. Diagram of standard oxidation-reduction potentials (in volts)

ganate ion $E^{\circ}_{MnO_4^-,\ H^+/Mn^{2+}} = 1.51$ V. Substances whose standard potential is lower than the potential of the system HNO_2, H^+/NO ($E^{\circ} = 0.99$ V) reduce the nitrite ion, for example, the iodide ion ($E^{\circ}_{I_3^-/3I^-} = 0.536$ V).

Reagents

Sodium nitrite, 1 per cent solution.
Potassium iodide, 5 per cent solution.
Potassium permanganate, 0.1 per cent solution.
Acetic acid, 30 per cent solution.

Procedure. In a cylinder, put 100 ml of sodium nitrite solution, 200 ml of water and 20 ml of acetic acid solution. At the lecture, divide the solution into two parts. To one part, add 20 ml of potassium iodide solution. The separation of iodine and brown gas is observed. To the other part, add the potassium permanganate solution. The pink colour of permanganate disappears as it is added to the sodium nitrite solution.

Effect of the Hydrogen Ion Concentration on the Oxidation-Reduction Potential

Experiment 96. Reaction Between Nitrite and Iodide Ions

In acid solutions, the iodide ion is oxidized by the nitrite ion

$$2NO_2^- + 3I^- + 4H^+ \rightleftarrows I_3^- + 2NO\uparrow + 2H_2O$$

$$E^{\circ}_{HNO_2,\ H^+/NO} = 0.99\ V \qquad E^{\circ}_{I_3^-/3I^-} = 0.536\ V$$

At pH $>$ 6, the redox potential of the system HNO_2, H^+/NO decreases so greatly that iodide oxidation reaction is impossible.

In the quantitative determination of the nitrite ion, for acidifying a solution, use may be made of acids whose ionization constants are lower than the ionization constant of nitrous acid ($pK_{HNO_2} = 3.22$), since nitrous acid decomposes according to the equation:

$$3HNO_2 \rightleftarrows H^+ + NO_3^- + 2NO\uparrow + H_2O$$

Reagents
Sodium nitrite, 1 per cent solution.
Potassium iodide, 5 per cent solution.
Acetic acid, 2 *M* solution.

Procedure. In a cylinder, put 100 ml of sodium nitrite solution and 200 ml of water. At the lecture, divide the solution into two parts. To the first part, add 50 ml of potassium iodide solution. No changes are observed. To the second part, add 50 ml of acetic acid solution and 50 ml of potassium iodide solution; iodine is formed.

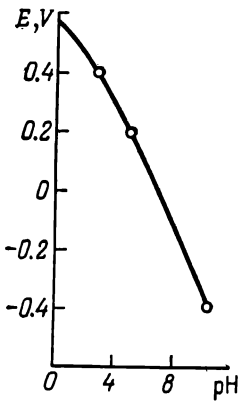


Fig. VIII-3. Dependence of the potential on the pH for the arsenate ion-arsenite ion system

Experiment 97. Reaction of Iodine with Arsenous Acid

The arsenic acid reduction by the iodide ion proceeds quantitatively when the concentration of mineral acid is not less than 4 *M*.

The following equation may be written for the reaction of arsenous acid oxidation by iodine at pH $\leqslant$ 2:

$$HAsO_2 + I_3^- + 2H_2O \rightleftarrows H_3AsO_4 + 3I^- + 2H^+$$

The equilibrium constant of the reaction is $5.5 \cdot 10^{-2}$. In the pH range of 5-14, the following equilibrium occurs (Fig. VIII-3)

$$HAsO_2 + I_3^- + 2H_2O \rightleftarrows HAsO_4^{2-} + 3I^- + 4H^+$$

The ionization constant of arsenous acid is $pK_1 = 9.2$; for arsenic acid, $pK_1 = 2.2$; $pK_2 = 6.9$ and $pK_3 = 11.5$ (25° C, $\mu \to 0$).

Reagents
Arsenous acid, 1 per cent solution.
Iodine, 1 per cent solution (see Experiment 7)
Sulphuric acid, 4 *M* solution.
Sodium hydrocarbonate, saturated solution.

Procedure. In a cylinder, put 20 ml of arsenous acid solution, 10 ml of sulphuric acid solution and 200 ml of

water. At the lecture, pour in 20 ml of iodine solution. The solution assumes the yellow colour of iodine. Add 50 ml of sodium hydrocarbonate solution; the solution is decoloured. Add 50 ml of sulphuric acid solution; a yellow colour reappears.

Change in the Oxidation-Reduction Potential by Complex Formation

Experiment 98. Change in the Potential of the Cobaltic-Cobaltous System in the Presence of Ammonia

In aqueous solutions, the cobaltous ion is not oxidized to the cobaltic ion by oxygen, since $E^{\circ}_{Co^{3+}/Co^{2+}} = 1.84$ V, and $E^{\circ}_{O_2,\ H/H_2O} = 1.23$ V. In the presence of complexing agents, such as ammonia, which forms with cobaltic ions more stable complexes than with cobaltous ions, oxidation by oxygen is possible, since $E^{\circ}_{[Co(NH_3)_6]^{3+}/[Co(NH_3)_6]^{2+}} = 0.1$ V:

$$2[Co(NH_3)_6]^{2+} + {}^1/_2O_2 + H_2O \rightleftarrows 2[Co(NH_3)_6]^{3+} + 2OH^-$$

dirty yellow — cherry red

$\log \beta_6 = 4.39$ — $\log \beta_6 = 33.66$

(25° C, $\mu \to 0$)

Equipment and Reagents

Oxygen bubbler.
Oxygen tank.
Cobaltous chloride, 1 per cent solution.
Ammonia, 25 per cent solution.

Procedure. In a cylinder, put 10 ml of cobalt chloride solution and 200 ml of water. Add the ammonia solution until the dark blue precipitate of basic salts is dissolved and a complex of dirty yellow colour is formed. Bubble oxygen through the solution. A change in the colour of the solution to cherry red is observed.

Note. If air is led up to the demonstration table in the auditorium, it may be bubbled through the solution.

Experiment 99. Change in the Potential of the Ferric-Ferrous System in the Presence of Fluoride Ions (Reaction of Iodide Ion Oxidation)

The ferric-ferrous system in an aqueous solution is a graphic example of the effect of complexing agents on the relative stability of ions of different degrees of oxidation. Ferric ions tend to form stronger complexes than ferrous

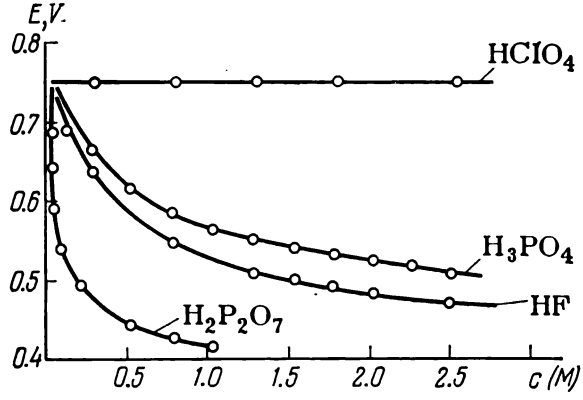


Fig. VIII-4. Change in the potential of the ferric-ferrous system in the presence of complexing agents

ions, owing to which E^f diminishes in the presence of complexing agents (Fig. VIII-4). Hence, $E^{\circ}_{Fe^{3+}/Fe^{2+}} = 0.77$ V, in 1 *M* HF

$E^f_{[FeF_n]^{(3-n)+}/Fe^{2+}} = 0.32$ V. A decrease in the potential

entails a change in the direction of the reaction of iodide ion oxidation by the ferric ion, $E^{\circ}_{I_3^-/3I^-} = 0.536$ V:

$$2Fe^{3+} + 3I^- \rightleftarrows 2Fe^{2+} + I_3^-$$

As complexing agents, use may be made of not only fluoride ions ($[FeF_4]^-$, $\log \beta_3 = 11.86$, $\mu = 0.5$), but also of tartaric acid ($[Fe(C_4H_4O_6)_2]^-$, $\log \beta_2 = 11.86$), ethylenediaminetetra-acetic acid ($[FeY]^-$, $\log \beta_1 = 25.1$, $\mu = 0.1$) and oxalic acid ($[Fe(C_2O_4)_3]^{3-}$, $\log \beta_3 = 20.46$, $\mu = 0.5$).

Reagents

Ferric chloride, 0.1 per cent solution in 0.1 *N* hydrochloric acid solution.

Potassium iodide, 10 per cent solution.

Sodium fluoride, saturated solution in a polyethylene bottle.

Procedure. In a cylinder, put 400 ml of iron chloride solution. At the lecture, divide the solution into two parts. To one part, add 50 ml of potassium iodide solution. Iodine is separated, and the solution becomes brown. To the other part, add 100 ml of sodium fluoride solution and note the disappearance of the faint yellow colour that is characteristic of ferric chloride complexes. Add 50 ml of potassium iodide solution. Iodine is not separated.

Note. The solution of tartaric, oxalic or ethylenediaminetetraacetic acids may be used instead of a sodium fluoride solution.

Experiment 100. Change in the Potential of the Ferric-Ferrous System in the Presence of Fluoride Ions (Reaction of Silver Ion Reduction)

As we have seen in the previous experiment, in the presence of fluoride ions, E^f of the ferric-ferrous system diminishes so greatly that the ferrous ion becomes a comparatively strong reducing agent, $E^f \leqslant 0.32$ V. As a result, a reaction of silver ion reduction to metal silver may occur $E^\circ_{Ag^+/Ag\downarrow} = 0.80$ V:

$$Ag^+ + Fe^{2+} + 4F^- \rightleftarrows Ag\downarrow + [FeF_4]^-$$

Reagents

Mohr's salt, 1 per cent solution in 0.2 *N* sulphuric acid solution.

Silver nitrite, 1 per cent solution.

Sodium fluoride, saturated solution.

Procedure. In a cylinder, put 300 ml of Mohr's salt solution. At the lecture, add 10-20 ml of silver nitrite solution. No changes are observed. Add 50 ml of sodium fluoride solution; metal silver is separated. The solution becomes turbid, gray-green, and then dark. Partial coagulation of

silver occurs in the course of time. The silver precipitate may be filtered, and then ground with a pestle on a filter, producing a lustrous surface.

Note. Like in the previous experiment, other complexing agents may be used.

Experiment 101. Change in the Potential of the Molybdenum (VI)-Molybdenum (V) System in the Presence of Phosphate Ions

The molybdate ion is not reduced by sodium sulphite in a strongly acid medium (more than 0.5 *M* H_2SO_4). In the presence of phosphate ions, a molybdophosphoric heteropoly acid is formed with a higher potential:

$$E^{f}_{Mo^{VI}/Mo^{V}} = 0.53\ V,\quad E^{f}_{[PMo_{12}O_{40}]^{3-}/[PMo^{VI}_{10}Mo^{V}_{2}O_{40}]^{5-}} = 0.76\ V.$$

The heteropoly anion of yellow colour is reduced by sodium sulphite with the formation of blue molybdophosphoric acid.

Reagents

Sodium molybdate, 10 per cent solution.
Monopotassium phosphate, 0.1 per cent solution.
Sodium sulphite, 1 per cent solution.
Sulphuric acid, 2 *M* solution.

Procedure. In a cylinder, put 400 ml of water, 50 ml of sodium molybdate solution and 150 ml of 2 *M* sulphuric acid solution. Divide the solution into two parts. To one part, add 20 ml of sodium sulphite solution; no changes occur. To the other part, add 30 ml of potassium phosphate solution and stir. The yellow colour of the heteropoly complex appears. Add 20 ml of sodium sulphite solution. The colour of the solution becomes intense dark blue.

Experiment 102. Change in the Potential of the Cupric-Cuprous System in the Presence of EDTA

When cupric ions react with iodide ions, cupric ions are reduced to cuprous ions with the formation of slightly soluble cuprous iodide: $E^{\circ}_{I^{3-}/3I^{-}} = 0.536\ V$, $E^{\circ}_{Cu^{2+}/CuI} = 0.86\ V$.

If cupric ions are bound into a complex with EDTA, the oxidation of the iodide ion becomes impossible ($\log K_{Cu\,Y^{2-}} = 18.80$, $\mu = 0.1$).

Reagents
Cupric sulphate, 1 per cent solution.
Potassium iodide, 5 per cent solution.
EDTA, saturated solution.

Procedure. In a cylinder, put 50 ml of copper sulphate solution and 300 ml of water. At the lecture, divide the solution into two parts. To one part, add 30 ml of potassium iodide solution. The solution becomes brown owing to the formation of iodine, and a precipitate is formed. To the other part, add 100 ml of EDTA solution. A dark blue cupric complex is formed. Add 30 ml of potassium iodide solution. The formation of iodine and the separation of a precipitate are not observed.

STEPWISE OXIDATION-REDUCTION REACTIONS

Oxidation-reduction reactions often proceed through intermediate stages. This is characteristic of elements that exist with several degrees of oxidation. For example, vanadium has different degrees of oxidation (V, IV, III, II). Therefore, reactions of vanadium (V) reduction or vanadium (II) oxidation proceed stepwise with the formation of intermediate ions that have a characteristic colour. Oxidation-reduction reactions of vanadium salts occur in an acid medium. Attention should be drawn to the fact that in a sulphuric acid medium, vanadium (V) forms VO_2^+ ions of yellow colour and several polymer ions of greater complexity (Table IV-2):

$$VO_3^- + 2H^+ \rightleftarrows VO_2^+ + H_2O$$

On reduction, the vanadium (IV) ion is first produced in the form of aquo vanadyl $[VO(H_2O)_5]^{2+}$ of blue colour:

$$VO_2^+ + 2H^+ + 4H_2O + \bar{e} \rightleftarrows [VO(H_2O)_5]^{2+} \quad E^\circ = 1.0\ V$$

Further the vanadium (III) ion is produced in the form of aquo ions $[V(H_2O)_6]^{3+}$ of green colour:

$$[VO(H_2O)_5]^{2+} + 2H^+ + \bar{e} \rightleftarrows [V(H_2O)_6]^{3+} \quad E^\circ = 0.36V$$

Finally, the vanadium (II) ion is produced in the form of aquo ions $[V(H_2O)_6]^{2+}$ of violet colour:

$$[V(H_2O)_6]^{3+} + \bar{e} \rightleftarrows [V(H_2O)_6]^{2+} \quad E^\circ = 0.25V$$

If the ions $[V(H_2O)_6]^{2+}$ and $[VO(H_2O)_5]^{2+}$ are simultaneously present in the solution, an intermediate compound of brown colour that has the bridged group $[VOV]^{4+}$ may be formed. Vanadium (II) is oxidized through the same stages in a reverse order. When $[VO(H_2O)_5]^{2+}$ is formed, partial direct oxidation and partial oxidation through the intermediate $[VOV]^{4+}$ may occur.

Experiment 103. Reduction of Vanadate

Metals may be used for demonstrating the stepwise reduction of vanadate ions.

Reagents
Ammonium vanadate, 0.5 per cent solution.
Sulphuric acid, 9 *M* solution.
Granulated zinc.

Procedure. In a cylinder, put 200 ml of a colourless solution of ammonium vanadate. At the lecture, add 20 ml of sulphuric acid. Draw the attention of the audience to the fact that the solution assumes a yellow colour, which is characteristic of VO_2^+ ions. Add 20 g of zinc. Under the action of hydrogen that is being evoluted, the colour gradually changes to blue, and then to green, and finally to lilac. Somewhat later, the solution becomes brown.

Experiment 104. Oxidation of a Vanadium (II)

The previous experiment may be carried out reversely, observing the intermediate stages of vanadium oxidation. Potassium permanganate or ceric sulphate may be used as an oxidizing agent.

Reagents

Vanadium (II) sulphate, 0.5 per cent solution in 1 *M* sulphuric acid solution. The solution produced in the previous experiment may be used.

Potassium permanganate or ceric sulphate, 0.04 *N* solution.

Procedure. A lilac solution of vanadium sulphate produced in the previous experiment is poured into a cylinder, and cerium sulphate solution is slowly added from a burette, observing the gradual colour change from lilac through green and blue to yellow.

MASKING BY CHANGING THE DEGREE OF OXIDATION OF ELEMENTS

Experiment 105. Masking Iron (III) by Changing the Degree of Its Oxidation

The cobaltous ion forms with thiocyanate ions, a complex that has a blue colour in an aqueous-organic medium (acetone, ethanol or methanol); see Experiment 38:

$$[Co(H_2O)_6]^{2+} + n NCS^- \rightleftarrows [Co(NCS)_n(H_2O)_{6-n}]^{(n-2)-} + n H_2O$$

Ferric ions interfere with the detection of cobalt ions by this reaction, forming red complexes with thiocyanate ions (see Experiment 36). However, the cobaltous ion may be detected in the presence of the ferric ion by reducing the latter to a valence of two by a suitable reducing agent, such as tin dichloride:

$$2Fe^{3+} + [SnCl_4]^{2-} + 2Cl^- \rightleftarrows 2Fe^{2+} + [SnCl_6]^{2-}$$

Reagents

Cobaltous chloride, 0.1 per cent solution.

Ferric chloride, 0.01 per cent solution in 0.1 *N* hydrochloric acid solution.

Ammonium thiocyanate, 10 per cent solution.

Tin chloride, 2 per cent solution in 1 *M* hydrochloric acid solution.

Acetone.
Sulphuric acid, solution 1 : 1.

Procedure. In a cylinder, put 10 ml of cobalt chloride solution, 1 ml of iron chloride solution, 5 ml of sulphuric acid solution, 30 ml of water and 150 ml of acetone. At the lecture, add 30 ml of ammonium thiocyanate solution. A mixed dirty-brown colour appears. Add 20 ml of tin chloride solution. A bright blue colour of cobalt thiocyanate is observed (use white screen!).

OXIDATION-REDUCTION INDICATORS

The end point of titration in oxidation-reduction titration may be recorded in several ways: when titrant colour appears or disappears, by utilizing substances which specifically react with one of the forms of an oxidation-reduction pair, or substances which are themselves subjected to oxidation and reduction and produce oxidized and reduced forms that have a different colour (redox indicators).

A redox indicator is an oxidation-reduction system, either reversible or irreversible. For reversible indicators, the following equation is valid:

$$\mathrm{Ind_{Ox}} + n\bar{e} \rightleftarrows \mathrm{Ind_{Red}}$$

where $\mathrm{Ind_{Ox}}$ and $\mathrm{Ind_{Red}}$ = oxidized and reduced forms of the indicator.

If the colour intensity of both forms of the indicator is approximately the same, the transition range of the colour is calculated by the formula (at 25° C):

$$E = E^{\mathrm{f}} \pm \frac{0.059}{n}$$

As irreversible redox indicators, use is made of methyl orange, fuchsin, and so forth, which are irreversibly destroyed at the end point of titration [4]. Chemiluminescent indicators (luminol, lucigenin), which are irreversibly oxidized with light emission, and fluorescent indicators, may likewise be used.

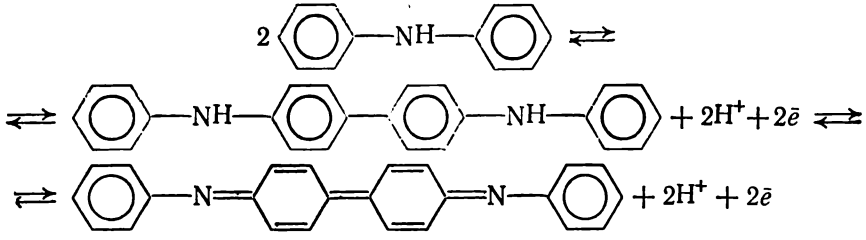
Indicator	E^{o}, V	*Transition range, V* 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4
Neutral red	0.24	C▨R
Methylene blue	0.53	C▨D
Diphenylamine	0.76	C▨V
O-Dianisidine	0.85	C▨R
Eriogluein A	1.00	G▨R
Ferroin	1.06	R▨B
Phenylanthranilic acid	1.26	C▨R
2,2'-Dipyridyl - Ru^{IV}	1.33	y▨C

B=blue, C=colourless, D=dark blue, G=green, R=red, V=violet, Y=yellow

The listeners should be shown a table of redox indicators with the range of colour change potentials.

Experiment 106. Titration of Iron (II) by Cerium (IV) in the Presence of Diphenylamine

Colourless diphenylamine is oxidized first to colourless diphenylbenzidine, and then to violet diphenylbenzidine



When a large excess of an oxidizing agent is added, violet diphenylbenzidine is subjected to further oxidation with the formation of red and yellow products of an uncertain composition.

Diphenylamine ($E^\circ = 0.76$ V) may be used in many reactions, for example, in titrating ceric salts by ferrous salts

$$Ce^{4+} + Fe^{2+} \rightleftarrows Fe^{3+} + Ce^{3+}$$

Ceric salts have a yellow colour. Titration may be conducted also without an indicator, determining the equivalence point at the disappearance of yellow colour. However, such a transition is not clearly-defined in dilute solutions. The addition of an indicator considerably increases the accuracy of titration.

Reagents

Mohr's salt. 0.1 *N* solution in 0.2 *N* sulphuric acid solution.

Ceric sulphate, 0.1 *N* solution in 0.5 *M* sulphuric acid solution.

Diphenylamine, 1 per cent solution in concentrated phosphoric acid.

Procedure. Take two cylinders and in each of them put 200 ml of water and 4 ml of cerium sulphate solution. The solutions have a faint yellow colour. Titrate the first solution by Mohr's salt solution until it becomes colourless. Draw the listeners' attention to the fact that the equivalence point is hardly noticeable. To the second solution, add a diphenylamine indicator. The solution becomes intense dark blue. Titrate with Mohr's salt until the dark blue colour disappears.

Experiment 107. Titration of Iron (II) by Cerium (IV) in the Presence of 1,10-Phenanthroline

The base 1,10-phenanthroline forms with the ferrous ion a complex of an intense red colour (ferroin). Under the action of strong oxidizing agents, iron (II) in a complex is oxidized to iron (III). The complex of iron (III) with 1,10-phenanthroline has a pale blue colour:

$$[Fe(C_{12}H_8N_2)_3]^{2+} \rightleftarrows [Fe(C_{12}H_8N_2)_3]^{3+} + \bar{e}$$

The oxidized form is resistant to the action of oxidizing agents. The reaction is reversible, $E^\circ = 1.06$ V. A colour

change is observed when the potential is about 1.12 V (Fig. VIII-5).

Reagents

Ferrous sulphate, 0.1 *N* solution in 2 *M* sulphuric acid solution.

Ceric sulphate, 0.1 *N* solution in 0.5 *M* sulphuric acid solution.

1,10-phenanthroline.

Procedure. In a cylinder, put 2 ml of iron sulphate solution and 500 ml of water. Add about 50 mg of 1,10-phenanthroline and stir. The solution becomes red. Divide the

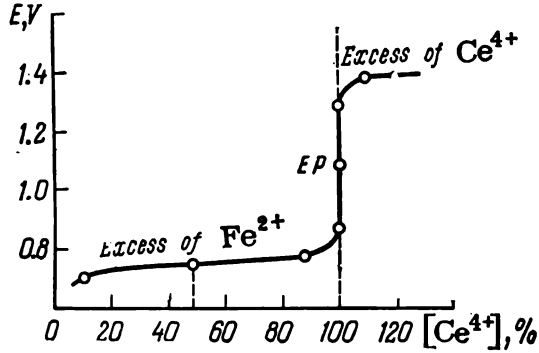


Fig. VIII-5. Titration curve of 0.1N iron (II) solution by 0.1N cerium (IV) solution (H_2SO_4)

solution into two parts. Keep one part for reference. To the other part, add 20 ml of cerium sulphate solution. The colour changes to blue.

Experiment 108. Effect of Temperature in Iodometric Titration in the Presence of Starch as Indicator

Starch is an indicator which specifically reacts with iodine. Two processes occur when starch and other polysaccharides react with iodine: complex formation, which is subordinated to stoichiometric relations, and adsorption. The first to enter into a reaction is amylose, a component of starch. The amylose chain in the form of a spiral winds around iodine molecules, which are distributed along the spiral axis. In this case, there are six glucose residues per

iodine molecule (Fig. VIII-6) [5]. The reaction is reversible, and the temperature strongly affects equilibrium.

Reagents
Iodine, 0.01 *N* solution.
Starch, 1 per cent aqueous solution.

Procedure. Put a starch solution in a test tube with a diameter of 3 cm and a length of 16-20 cm. At the lecture, add several drops of an iodine solution until a dark blue

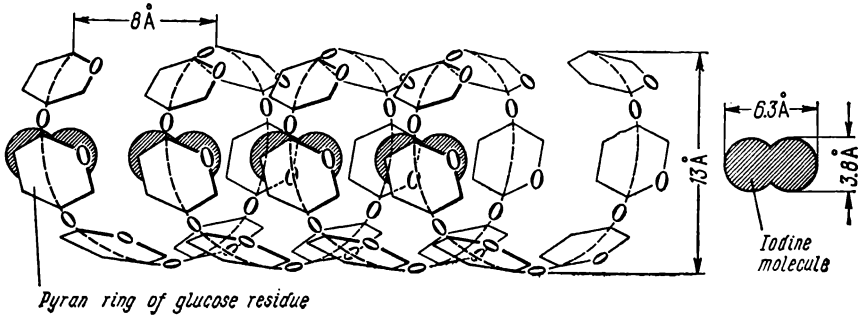


Fig. VIII-6. Structure diagram of a complex of amylose with iodine

colour appears. Immerse the test tube into a beaker with boiling water. In this case, the solution becomes colourless. Take out the test tube and cool it. The dark blue colour is restored.

Experiment 109. Titration of Arsenite by Hydrogen Peroxide in the Presence of a Chemiluminescent Indicator

The arsenite ion is oxidized by hydrogen peroxide in an alkaline medium:

$$AsO_2^- + H_2O_2 + OH^- \rightleftarrows HAsO_4^{2-} + H_2O$$

An excess of hydrogen peroxide in an alkaline medium oxidizes luminol or lucigenin; therefore, there is an intense glow after the attainment of the equivalence point (see Experiment 29) [6].

Reagents
Sodium arsenite, 0.001 *N* solution.
Hydrogen peroxide, 0.1 *N* solution.
Sodium hydroxide, 0.1 *N* solution.
Luminol, 0.5 per cent solution.

Procedure. In a conical 1-litre flask, put 50 ml of sodium arsenite solution and add 50 ml of alkaline solution and 400 ml of water. At the lecture, add 5 ml of indicator solution. Switch off the light and darken the auditorium. In the dark, very slowly add a hydrogen peroxide solution from a burette until blue luminescence appears.

Experiment 110. Titration of Iron (II) by Potassium Permanganate in the Presence of Rhodamine B as Fluorescent Indicator

Redox fluorescent indicators change the intensity or colour of fluorescence when the potential of the solution is changed. The change in fluorescence is connected with the oxidation or reduction of an indicator: the oxidized or reduced form of the indicator fluoresces. An advantage of such indicators is that they may be used for titration in turbid and coloured solutions. For example, iron cannot be determined permanganatometrically in coloured solutions. However, the utilization of Rhodamine B makes it possible to determine iron by this method [7].

Reagents
Mohr's salt, 0.05 *N* solution in 0.2 *N* sulphuric acid solution.
Potassium permanganate, 0.05 *N* solution.
Sulphuric acid, 1 *M* solution.
Rhodamine B, 0.1 per cent aqueous solution.
Colour India ink.

Procedure. In a conical 300-ml flask, put 5 ml of Mohr's salt solution, 100 ml of sulphuric acid solution and 2-3 drops of India ink. At the lecture, add the indicator. Put the flask in the path of ultraviolet rays (Fig. V-3) and switch off the light. Rhodamine B has an orange-yellow glow. Titrate with the potassium permanganate solution until the extinction of fluorescence.

REACTION RATE AND CATALYTIC PROCESSES IN OXIDATION-REDUCTION REACTIONS

Oxidation-reduction reactions tend to proceed slowly and, as a rule, in many stages. In a multiple-stage reaction, unstable states of intermediate degrees of oxidation usually originate. The reaction rate is limited by the rate of the slowest stage. This reaction rate is very important in chemical analysis, especially in titrimetry. The slow

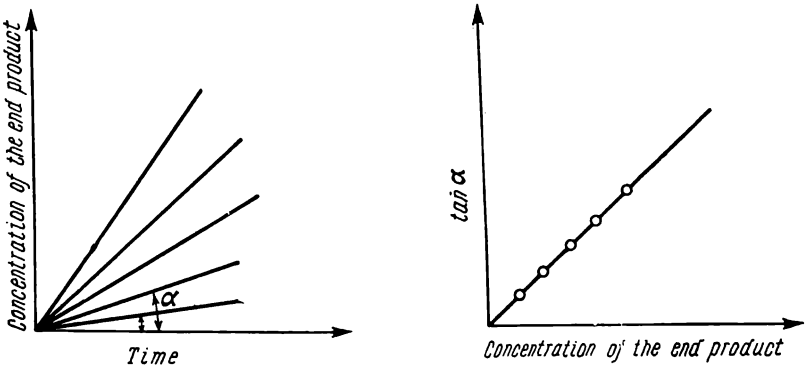


Fig. VIII-7. Change in the concentration of a substance in time

rate in the vicinity of the equivalence point often makes it difficult to use the reaction in quantitative analysis. The reaction rate is affected by many factors: temperature, concentration, medium, catalyst presence, and so forth (Fig. VIII-7) [8, 9].

Table

SENSITIVITY OF REACTIONS FOR DETERMINING ELEMENTS BY THE KINETIC METHOD

Ion	Reagents	Limit of detection, μg/ml
Fe^{3+}, Fe^{2+}	*n*-Phenetidine, hydrogen peroxide	10^{-4}
Co^{2+}	*n*-Tolidine, pyrocatechol, perborate	10^{-5}
Cu^{2+}	Luminol, hydrogen peroxide	10^{-4}
Ni^{2+}	Tiron, diphenylcarbazone, hydrogen peroxide	10^{-3}

The section "Reaction Rate and Catalytic Processes in Oxidation-Reduction Reactions" is expounded in a special lecture after considering the fundamental questions concerning oxidation-reduction reactions in titrimetric analysis.

It should be noted that catalytic reactions are used for quantitatively determining element traces (kinetic method of analysis); catalytic reactions are very sensitive (see the table) [8].

Effect of Ion Concentration on the Reaction Rate

Experiment 111. Dependence of the Induction Period on Reactant Concentration (Landolt's Reaction)

The iodate ion — sulphite ion reaction is characterized by a considerable induction period and proceeds in several stages [10]:

$$IO_3^- + 3SO_3^{2-} \rightleftarrows 3SO_4^{2-} + I^- \text{ (slowly)}$$

$$5I^- + IO_3^- + 6H^+ \rightleftarrows 3I_2 + 3H_2O \text{ (rapidly)}$$

$$I_2 + SO_3^{2-} + H_2O \rightleftarrows SO_4^{2-} + 2I^- + 2H^+ \text{ (rapidly)}$$

The last reaction occurs more rapidly than the second one; therefore, free iodine appears in the solution only after the oxidation of the entire sulphurous acid. The duration of the induction period depends on the concentration of parent substances; this makes it possible to use Landolt's reaction for quantitatively determining the iodate ion and the sulphite ion in a kinetic variant [11]. The concentration (x) of the iodate ion or the sulphite ion is connected with the induction period by the equation

$$x = c\left(\frac{t_c}{t_x}\right)^n$$

where

c = concentration of a standard solution;

t_c and t_x = induction periods for a standard solution and a solution being studied;

n = quantity which is constant for the given experimental conditions.

The sensitivity of determining the iodate ion is 200 μg/ml, and that of the sulphite ion is 100 μg/ml.

Reagents

Potassium iodate, 0.4 per cent solution.

Sodium sulphite, 0.1 per cent solution. One gram of sodium sulphite, 0.94 ml of concentrated sulphuric acid and 10-20 ml of 1 per cent starch solution are dissolved in one litre of water.

Procedure. Take three cylinders and in each of them put 100 ml of potassium iodate solution. Prepare beforehand three beakers containing 100 ml, 50 ml and 25 ml of sodium sulphite solution. Dilute the three solutions to the same volume with water. At the lecture, switch on the metronome (one stroke per second) and quickly pour the solution from the first beaker into the first cylinder. After several strokes, a dark blue colour suddenly appears. Into the second cylinder, pour the solution from the second beaker and count the number of strokes until the appearance of a dark blue colour. Do the same with the third beaker. The duration of the incubation period must be strictly proportional to the sulphite concentration.

Note. The experiment may be carried out with two cylinders. The mixtures from the first and second beakers may be poured simultaneously also into two cylinders and the duration of the incubation period may be counted. The duration should be regulated beforehand, depending on how much time a lecturer desires. For this purpose, the amount of the sodium sulphite solution may be changed.

Experiment 112. Interaction between Persulphate and Iodide Ions

In neutral and acid solutions, the persulphate ion reacts very slowly with the iodide ion:

$$S_2O_8^{2-} + 2I^- \rightleftarrows 2SO_4^{2-} + I_2$$

The reaction proceeds in several stages [12]:

$$I^- + S_2O_8^{2-} \rightleftarrows S_2O_8I^{3-}$$

being the reaction which controls the rate of the entire process

$$S_2O_8I^{3-} \rightleftarrows S_2O_8^{3-} + I$$
$$S_2O_8^{3-} + I^- \rightleftarrows 2SO_4^{2-} + I$$
$$S_2O_8I^{3-} + H_2O \rightleftarrows 2SO_4^{2-} + HOI + H^+$$

As we see, the time required for the completion of the entire process depends on the concentration of the iodide ion.

Reagents

Solution A. 16.6 g of potassium iodide and 0.02 g of sodium thiosulphate are dissolved in 500 ml of water, and a small amount of a starch solution is added.

Potassium persulphate, 0.025 *M* solution.

Procedure. Take three cylinders and put 150 ml of solution *A* in each of them. Prepare beforehand three beakers containing 150 ml of potassium persulphate solution (one beaker), 100 ml of potassium persulphate solution and 50 ml of water (another beaker), and 50 ml of potassium persulphate solution and 100 ml of water (third beaker). Alternately, pour together the contents of the cylinders and of each beaker (see the previous experiment), noting the time of appearance of the dark blue colour of the compound of iodine with starch (use a metronome).

Experiment 113. Destruction of Thiosulphate Ions in an Acid Medium

The thiosulphate ion is relatively stable in neutral and alkaline solutions. But if the hydrogen ion concentration exceeds $2.5 \cdot 10^{-5}$ M, very unstable hydrothiosulphate ions are formed; the decomposition mechanism of these ions is very complex, consisting in the formation of sulphur-bearing products (sulphite, sulphate, sulphide, tetrathionate, sulphur).

In weakly acid solutions, the main decomposition product is the pentathionate ion, which is slowly formed according to the equation:

$$5S_2O_3^{2-} + 6H^+ \rightleftarrows 2S_5O_6^{2-} + 3H_2O$$

The process of pentathionate decomposition is complex; one of the rapid reactions is decomposition into the tetrathionate ion and element sulphur.

The decomposition rate of the thiosulphate ion in an acid medium depends on the concentrations of thiosulphate ions and hydrogen ions.

Reagents

Sodium thiosulphate, 1 *M* solution.

Hydrochloric acid, 1 *M* solution.

Procedure. In three cylinders, put 10 ml, 20 ml and 40 ml of sodium thiosulphate solution, respectively, and dilute to 200 ml with water. In three beakers, put 10 ml, 20 ml and 40 ml of hydrochloric acid solution, respectively, and dilute to 50 ml. At the lecture, quickly mix the respective solutions of the cylinders and beakers alternately, noting by the metronome the time of appearance of opalescence against a black screen.

Catalytic and Induced Reactions

The rate of chemical reactions sharply changes in the presence of catalysts. In addition, the equilibrium constant does not change. Catalyst participation in a reaction is of a cyclic nature. As a result of a cycle, the parent substances become new substances, and the catalyst which initially participated in a reaction is regenerated. Every cycle consists of several stages. The overall rate is controlled by the rate of the slowest stage. The reaction rate constant increases in most cases owing to a decrease in the activation energy during catalyst action.

In analysis, the most common methods are those based on the utilization of homogeneous catalysis of oxidation-reduction reactions.

Apart from catalytic reactions, induced reactions are used. The "chemical induction" phenomenon consists in the fact that a reaction (induced) which proceeds very slowly under the given conditions is caused only by the simultaneous occurrence of another reaction (primary). There are two classes of induced reactions: induced chain and conjugate reactions, which differ from one another by

the nature of the change in the induction factor F_i [1]:

$$F_i = \frac{\text{number of equivalents in the induced reaction}}{\text{number of equivalents in the primary reaction}}$$

The induction factor of conjugate reactions approximates a certain small value, while it infinitely increases for chain reactions.

In analysis, conjugate reactions are mainly used. Induced chain reactions, which do not give reliable quantitative data, may be a source of errors.

Experiment 114. Reaction of Thiosulphate Ion Oxidation by Hydrogen Peroxide in the Presence of Molybdate

The oxidation of the thiosulphate ion to the sulphate ion by hydrogen peroxide proceeds very slowly:

$$S_2O_3^{2-} + 4H_2O_2 \rightleftarrows 2SO_4^{2-} + 2H^+ + 3H_2O$$

The reaction rate sharply increases in the presence of the salts of some elements of the highest degree of oxidation: molybdenum (VI), vanadium (V), tungsten (VI), titanium (IV), etc. The mechanism of catalyst action is questionable. The following arrangement in which a complex (compound-catalyst) participates is possible; complex formation is apparently necessary but inadequate [8]:

$$K + H_2O_2 \rightleftarrows KO_2H_2$$
$$KO_2H_2 \rightleftarrows KOH^- + OH^+$$
$$KO_2H_2 \rightleftarrows KOH^- + H^+ + \cdot O$$
$$H^+ + KOH^- \rightleftarrows K + H_2O$$

where K = catalyst.

Oxidation in acid and alkaline media proceeds according to different mechanisms. However, in both cases, the oxidizing agent is not a molecule of hydrogen peroxide, but the ions and radicals OH^+, $\cdot O$, $\cdot OH$, $\cdot O_2H$ that are being formed.

Reagents

Sodium thiosulphate, 1 per cent solution.
Barium chloride, 5 per cent solution.
Sodium molybdate, 1 per cent solution.
Hydrogen peroxide, 3 per cent solution.

Procedure. In a cylinder, put 50 ml of sodium thiosulphate solution and 150 ml of water. At the lecture, add 40-50 ml of hydrogen peroxide solution and 20 ml of barium chloride solution. The sulphate ion is not formed in noticeable amounts, and the precipitation of barium sulphate is not observed. Add 30 ml of sodium molybdate solution. The solution immediately becomes turbid and a white precipitate of barium sulphate is formed. Observe how the solution grows turbid against a black screen.

Note. For the experiment to be successful, it is necessary to use chemical purity reagents and water which has been distilled twice.

Experiment 115. Autocatalytic Oxidation of Oxalic Acid by Potassium Permanganate

An induced reaction of oxalate oxidation by potassium permanganate is rather complex. The reaction mechanism has still not been completely clarified. In all probability, the reaction is conjugate; in addition, manganese (II) plays the role of an inductor (therefore, the reaction is related to the autocatalytic type). In the absence of manganese (II), the reaction is characterized by a long induction period during which manganese ions with different degrees of oxidation accumulate. In the presence of manganese (II), the reaction proceeds practically instantaneously. Apparently, the following process pattern is the most probable one [12]:

(1) $2MnO_4^- + 3Mn^{2+} + 16H^+ \rightleftarrows 5Mn^{4+} + 8H_2O$	rapid reaction
(2) $Mn^{4+} + Mn^{2+} \rightleftarrows 2Mn^{3+}$	rapid reaction
(3) $Mn^{4+} + C_2O_4^{2-} \rightleftarrows Mn^{3+} + CO_2 + \cdot CO_2^-$	reaction at a measurable rate
(4) $Mn^{4+} + \cdot CO_2^- \rightleftarrows CO_2 + Mn^{3+}$	rapid reaction
(5) $Mn^{3+} + 2C_2O_4^{2-} \rightleftarrows [Mn(C_2O_4)_2]^-$	rapid reaction
(6) $Mn^{3+} + C_2O_4^{2-} \rightleftarrows Mn^{2+} + CO_2 + \cdot CO_2^-$	reaction at a measurable rate
(7) $Mn^{3+} + \cdot CO_2^- \rightleftarrows Mn^{2+} + CO_2$	rapid but slower than the fourth reaction

Apart from the given complex with oxalate ions, manganese (III) forms also complexes having the composition $[Mn(C_2O_4)]^+$ and $[Mn(C_2O_4)_3]^{3-}$, which decompose at a measurable rate and retard oxidation-reduction reactions

Reagents

Oxalic acid, saturated solution.
Potassium permanganate, 0.01 *N* solution.
Manganese sulphate, 20 per cent solution.

Procedure. In a cylinder, put 200 ml of potassium permanganate solution and 200 ml of water. At the lecture, divide the solution into two parts. To one part, add an oxalic acid solution. The colour does not change. To the other part, add the same amount of oxalic acid and 50 ml of manganese sulphate solution. The solution becomes brown, then yellow, and finally it is completely decoloured. Note that in approximately one hour, the solution in the first cylinder is also decoloured.

Note. For the lecture experiment to be successful, an equal amount of 9 *M* sulphuric acid solution should be added to the manganese sulphate solution.

Experiment 116. Conjugate Reaction of Chloride Ion Oxidation by Permanganate Ions in the Presence of Ferrous Ions

In hydrochloric acid solutions, the reaction between the ferrous ion and the permanganate ion induces a reaction between the permanganate ion and the chloride ion. The induced oxidation of chloride ions is due to the formation of active intermediates of manganese with different degrees of oxidation (Mn^{3+}, Mn^{4+}, Mn^{5+}). The system that determines the potential is the Mn^{3+}/Mn^{2+} pair. It has been proved that the reduction of the permanganate ion necessarily passes through the stage of Mn^{3+} formation. The most probable mechanism of induced oxidation of the chloride ion is the following [I]:

$$MnCl^{2+} + Cl^- \rightleftarrows Mn^{2+} + \cdot Cl_2^-$$

$$\cdot Cl_2^- + Fe^{2+} \rightleftarrows Fe^{3+} + 2Cl^-$$

$$\cdot Cl_2^- + Mn^{3+} \rightleftarrows Mn^{2+} + Cl_2$$

The reaction of free chlorine formation is a source of errors in the permanganatometric determination of reducing agents which bring about the formation of noticeable amounts of manganese (III) but which do not form complexes with it. Substances that are capable of forming complexes with manganese (III), i.e., phosphates, sulphates, borates, and so forth, reduce the potential of the Mn^{3+}/Mn^{2+} system and prevent the oxidation of the chloride ion.

Reagents

Potassium permanganate, 0.1 *N* solution.
Ferrous sulphate, 0.1 *N* solution in 0.25 *M* sulphuric acid solution.
Manganese sulphate.
Hydrochloric acid, 0.1 *N* solution.
Potassium iodide, 2 per cent solution.
Starch, 1 per cent solution.
Carbon dioxide or *nitrogen.*

Procedure. Prepare two instruments, each of which consists of two vessels connected in series and a Kipp generator (Fig. VIII-8) [13]. In vessel *1* of each instrument, put

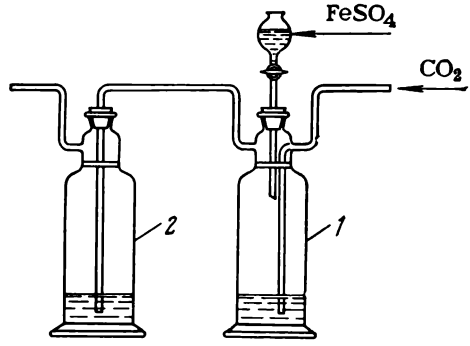


Fig. VIII-8. Instrument for the induced oxidation of the chloride ion by the permanganate ion

100 ml of hydrochloric acid solution and 1.5 ml of 0.1 *N* potassium permanganate solution. In vessel *2* of each instrument, put 50 ml of potassium iodide solution and 10 ml of starch solution. In a dropping funnel, put 1 ml

of 0.1 *N* ferrous sulphate solution. Pass a strong current of carbon dioxide from the Kipp generator, or a nitrogen current, through the system. There is no reaction between permanganate and chloride ions, chlorine is not formed, and changes in the second vessel are not observed. Add 1 ml of iron sulphate solution to vessel *1* of one of the instruments. In ten seconds, the solution in vessel *2* becomes dark blue due to the formation of a dark-blue iodine-starch complex from iodine that has been formed under the action of free chlorine. The solution in vessel *1* becomes brown due to the formation of manganese dioxide. Hence, the induced oxidation of chloride ions by permanganate ions has been effected.

To vessel *1* of the second instrument, add 400 mg of manganese sulphate and 1 ml of iron sulphate solution. The oxidation of chloride ions is not observed, and the solution in vessel *2* remains colourless.

Experiment 117. Reaction of Arsenous Ion Oxidation by Ceric Ions in the Presence of Iodide Ions

The reaction of arsenous ion oxidation by the ceric ion proceeds very slowly. The introduction of small amounts of iodide ions into a solution catalytically accelerates the reaction. The following sequence of stages with catalyst participation is possible:

$$Ce^{4+} + I^- \longrightarrow I + Ce^{3+}$$

$$2I \longrightarrow I_2$$

$$I_2 + H_2O \longrightarrow HOI + H^+ + I^-$$

$$H_3AsO_3 + HOI \longrightarrow H_3AsO_4 + H^+ + I^-$$

The method of iodide microdetermination has been worked out on the basis of the catalytic reaction of arsenite ion oxidation by the ceric ion. Osmium and ruthenium also considerably change the rate of this reaction [14].

Reagents

Cerium and ammonium nitrate, 0.02 *N* solution in 0.72 *M* sulphuric acid solution.

Sodium arsenite, solution containing 14.72 g of sodium arsenite and 70 ml of concentrated sulphuric acid in one litre.
Potassium iodide, dry.
Chloroform.

Procedure. In a cylinder, put a small crystal of potassium iodide and drown it with chloroform. From above, carefully pour a solution containing one volume of cerium nitrate solution and five volumes of sodium arsenite solution. Two phases are observed: a colourless organic phase and a yellow aqueous phase. Quickly shake the cylinder. The lower layer is coloured red-violet by iodine formed. Shake the cylinder once more; the decoloration of both phases is observed (Fig. VIII-9).

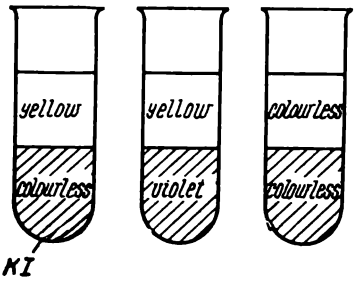


Fig. VIII-9. Demonstration of a catalytic reaction of arsenous ion oxidation by ceric ions

Experiment 118. Reaction of Thiosulphate Ion Oxidation by Ferric Ions

The thiosulphate ion is slowly oxidized by ferric ions according to the following simplified pattern:

$$2Fe^{3+} + 2S_2O_3^{2-} \rightleftarrows 2Fe^{2+} + S_4O_6^{2-}$$

The reaction is catalytically accelerated by cupric ions.

Reagents
Ferric chloride, 1 per cent solution in 0.1 *N* hydrochloric acid solution.
Sodium thiosulphate, 5 per cent solution.
Cupric sulphate, 0.1 per cent solution.

Procedure. In a cylinder, put 20 ml of ferric chloride solution and 300 ml of water. At the lecture, divide the solution into two parts. To one part, add 5 ml of copper sulphate solution. Add 20 ml of sodium thiosulphate solution to each of the two cylinders. The violet colour of a com-

plex of iron (III) with thiosulphate appears in both cylinders. However, the colour disappears very rapidly in the first cylinder, and slowly in the second one.

Experiment 119. Reaction of Hypophosphite Ion Oxidation by Iodine in the Presence of Thiosulphate Ions

The reaction of hypophosphite ion oxidation by iodine proceeds comparatively slowly. The reaction mechanism is complex and has not been completely clarified. The reaction is accelerated in the presence of compounds that contain bivalent sulphur (sulphides, thiosulphates) [15].

Reagents

Sodium hypophosphite, 0.08 *M* solution.
Sodium thiosulphate, 10^{-3} *M* solution.
Hydrochloric acid, 0.1 *N* solution.
Iodine, 0.04 *M* solution. 2.03 g of iodine and 10 g of potassium iodide are dissolved in 200 ml of water.

Procedure. In a cylinder, put 200 ml of sodium hypophosphite solution and add a few drops of hydrochloric acid (pH = 7). At the lecture, divide the solution into two parts. To one part, add 50 ml of iodine solution. To the other part, add 20 ml of sodium thiosulphate solution and 50 ml of iodine solution. Iodine is rapidly decoloured in the second cylinder, while decoloration occurs only in several minutes in the first one.

PHOTOCHEMICAL OXIDATION-REDUCTION

Some oxidation-reduction reactions are catalytically accelerated under the action of ultraviolet light. For example, iodine and iron (II), titanium (III) and uranium (IV) salts are rapidly oxidized by atmospheric oxygen in the sunlight. Such organic substances as glycerin, oxalic acid and methylene blue are reversibly oxidized by iron (III) under the action of ultraviolet radiation [16, 17].

Experiment 120. Reduction of Methylene Blue by Ferrous Ions under the Action of Ultraviolet Radiation

The action of ultraviolet radiation on a mixture of methylene blue and ferrous salts leads to the decoloration of the dye. This is due to the oxidation-reduction reaction whose equilibrium is displaced under the action of light towards the reduction of the dye and the oxidation of iron. The reaction is reversible.

Equipment and Reagents

Dark-blue lamp, 100-150 W.
Methylene blue, 0.05 per cent solution.
Ferrous sulphate, 2 per cent solution in 0.2 *M* sulphuric acid solution.

Procedure. In a flat-bottomed 1-litre flask, put 3 ml of methylene blue solution and 400 ml of water. At the lecture, add 100 ml of ferrous sulphate solution in an ordinary light. The colour of methylene blue does not change. Illuminate the solution with the dark-blue lamp. The colour disappears. Cover the flask with a dark hood. Remove the hood in ten minutes. The dark-blue colour is restored.

Note. See also Experiment 41.

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CHAPTER IX

Complexes in chemical analysis

Many metal ions form complexes with the most diverse ions and compounds. To explain the structure, stability and properties of coordination compounds, three theories are used: the valence bond theory, the electrostatic theory with regard to the effect of the crystalline field, and the molecular orbital theory. The molecular orbital theory is, at least in principle, the most general theory. It also takes account of a purely electrostatic interaction and may allow for any degree of covalence and π-bond. The molecular orbital theory explains such properties of complex compounds that are important in analytical practice as the stability of complexes, oxidation-reduction properties, spectra, and the kinetics of the complex formation [1-4]

The possibility of participation of certain orbitals of the central atom in complexation may be demonstrated by the data in Table IX-1 [5].

Table IX-1

PARTICIPATION OF THE ORBITALS OF THE CENTRAL ATOM IN COMPLEX FORMATION

Periods	Atomic orbitals				
	s	*p*	*d* (acceptor	*d* (donor)	*f*
1 H-He	+	−	−	−	−
2 Li-Ne	+	+	−	−	−
3 Na-Ar	+	+	+	−	−
4 K-Kr	+	+	+	+	−
5 Rb-Xe	+	+	+	+	−
6 Cs-Rn	+	+	+	+	+
7 Fr-Ku	+	+	+	+	+

If complex formation occurs only due to *s*-orbitals, σ-bonds originate; in complexing with the participation of *p*-orbitals, σ- and π-bonds originate; with the participation of *d*- and *f*-orbitals, σ- and π-bonds originate. When partially filled *d*- and *f*-orbitals of the central atom are present, there may be back π-bonds (in this case, the metal atom is an electron donor) and metal-metal bonds, and also cluster complex compounds.

The formation of certain types of chemical bonds of elements with different ligands may be illustrated by the following data [5]:

σ-Donor	NH_3, NR_3
σ, π-Donor	F^-, OH^-, H_2O, ROH, R_2O, complexones
σ, π-Donor with weak π-acceptor properties	Cl^-, Br^-, I^-, S^{2-}, R_3PO
σ-Donor and π-acceptor	CN^-, NO, PR_3
π-Donor and π-acceptor	C_2H_4, C_6H_6

The number of ligands in the inner coordination sphere depends on the nature of the ligand. For example, in the

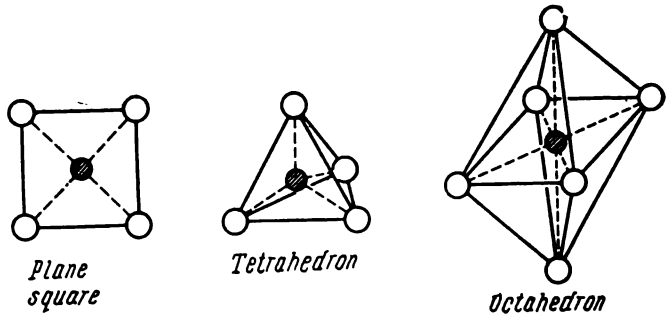


Fig. IX-1. Diagrams of crystal lattices of complex compounds

$[FeF_6]^{3-}$ and $[Fe(CN)_6]^{3-}$ complexes, the coordination number of iron (III) is six, and in the $[FeCl_4]^-$ complex, it is four. The coordination numbers may be two, four, six and more. Complexes with the coordination numbers of four

and six are most commonly found. It is expedient to demonstrate models of crystal lattices which show that four ligands in a complex are arranged either in the vertices of a tetrahedron or in the vertices of a plane square: $[Pt(NH_3)_2Cl_2]$, plane; $[Be(OH)_4]^{2-}$, tetrahedron; six ligands in a complex are arranged in the vertices of an octahedron: $K_2[PtCl_6]$, $K_2[SiF_6]$ (Fig. IX-1).

The coordination numbers and the "geometry" of complexes are given in Table IX-2 [5].

Table IX-2

COORDINATION NUMBERS AND "GEOMETRY" OF COMPLEXES FORMED BY DIFFERENT CENTRAL ATOMS

Periods	Coordination numbers								
	2	3	4 tetrahedron	5	6	4 square	7	8	9
1 H-He	+	—	—	—	—	—	—	—	—
2 Li-Ne	+	+	+	—	—	—	—	—	—
3 Na-Ar	+	+	+	+	+	—	—	—	—
4 K-Kr	+	+	+	+	+	+	+	+	—
5 Rb-Xe	+	+	+	+	+	+	+	+	+
6 Cs-Rn	+	+	+	+	+	+	+	+	+
7 Fr-Ku	+	+	+	+	+	+	+	+	+

Examples may be given to show that a change in the number of ligands in the inner and outer spheres of a complex changes its properties [6]:

$[Co(NH_3)_6]Cl_3$	Orange
$[Co(HN_3)_5Cl]Cl_2$	Purple
trans-$[Co(NH_3)_4Cl_2]Cl$ . . .	Green
cis-$[Co(NH_3)_4Cl_2]Cl$	Violet
$[Co(NH_3)_3Cl_3]$	Greenish-blue

Complexes are widely used for detecting ions, increasing the selectivity of reactions, and for masking and demasking ions, and also in different chemical and physicochemical methods of determining and separating elements. The most interesting and promising complexes are those of metal ions with complexones (polydentate ligands). The

utilization of complexones in analytical chemistry has enlarged the scope of titrimetric, gravimetric, optical, electrochemical and other analytical methods.

Various experiments may be shown at a lecture on the theory of complex formation. A description of only some experiments is given below; the experiments from other sections may also be used (see Experiments 10, 30, 31, 36, 38, 50, 67, 68, 98-102).

EFFECT OF THE STRUCTURE OF METAL ION AND LIGAND ON THE COLOUR OF COMPLEXES

Experiment 121. Colour of Aquo Compiexes of Metals

The aquo complexes of iron (II), cobalt (II), manganese (II), copper (II), nickel (II) and zinc have the same octahedral configuration, but they differ from one another by term splitting ΔE and, consequently, by colour (Table IX-3).

Table IX-3

COLOUR OF AQUO COMPLEXES OF METAL IONS

Ion	Filling of *d*-shell	Atomic number	ΔE, kcal/mol	Colour of aquo complex
Mn^{2+}	d^5	25	22.2	Colourless
Fe^{2+}	d^6	26	29.6	Yellow
Co^{2+}	d^7	27	26.5	Pink
Ni^{2+}	d^8	28	24.2	Green
Cu^{2+}	d^9	29	35.9	Dark blue
Zn^{2+}	d^{10}	30		Colourless

An aquo complex of zinc with a stable configuration of the *d*-shell is colourless. In the series Fe^{II}, Co^{II}, Ni^{II} and Mn^{II}, ΔE diminishes, being expressed in the shift of the absorption band into the long-wave region. The anomalous colour of copper (II) is connected with the distortion of the octahedral structure of the aquo complex [3].

Reagents

Sulphates of manganese (II), iron (II), cobalt (II), nickel (II), copper (II) and zinc, solid salts in jars with labels.

Procedure. Take six cylinders and pour 200-300 ml of water into each of them. To each cylinder, add 2 g of salts with a spatula and stir until they dissolve. Note that in spite of the same configuration of aquo complexes, the solutions of salts of different metals have a different colour.

Note. The solutions may be prepared beforehand, and cylinders with labels may be put on the table.

Experiment 122. Colour of Some Cobalt Complexes

The replacement of water molecules in aquo complexes of metals by other ligands is usually accompanied with the origination of a stronger ligand field; therefore, the difference of energies that corresponds to the *d-d* transition becomes larger, and the absorption maximum is shifted into the violet region. In this case, absorption intensity often grows possibly owing to a change in stereometry or to formation of charge-transfer complexes. The energy of splitting *d*-levels in the complexes of transition metals in respect to some of the most common ligands grows in sequence (spectrochemical series) [6]:

$$\underset{\text{weak ligand field}}{I^- < Br^- < Cl^- < OH^- \approx}$$

$$\underset{\text{medium ligand field}}{\approx F^- < H_2O < NCS^- < NH_3 < NO_2^- < \text{Phen}} \underset{\text{strong ligand field}}{< CN^-,\ CO}$$

Halide and thiocyanate complexes of iron (III) are charge-transfer ones that have intensive absorption bands. The transfer of the charge of a ligand to the metal is effected easier in the series $NCS^- > Br^- > Cl^-$; this is expressed in the deepening of colour in the series of $[FeCl_4]^-$, $[FeBr_4]^-$ and $[Fe(NCS)_4]^-$ complexes (see Experiment 2). The deepening of colour in the series of the copper (II) complexes $[CuCl_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$ and $Cu_2[Fe(CN)_6]$ is explained in a similar way (see Experiment 1).

According to the spectrochemical series, the force of an oxygen-containing ligand field is less than that of a nitrogen-containing ligand field. This is manifested in the colour change of complex ions of cobalt with the acetate ion, ammonia, and the nitrite ion: $[Co(H_2O)_6]^{2+}$, $[Co(CH_3COO)_2]$, $[Co(NH_3)_6]^{2+}$ and $[Co(NO_2)_6]^{3-}$.

Reagents

Cobaltous chloride, 10 per cent solution.
Sodium acetate.
Sodium nitrite.
Ammonia, 25 per cent solution.

Procedure. Take four cylinders and into each of them pour 100 ml of cobalt chloride solution. To one cylinder, add 100 ml of water, to another, 10 g of sodium acetate, to the third, 100 ml of ammonia solution, and to the fourth, 10 g of sodium nitrite. The complexes that are formed have a different colour: pink, bright pink, brown-pink and orange, respectively.

DISSOCIATION AND FORMATION OF COMPLEXES

Complexes are formed in aqueous solutions according to the following equations:

$$[M(H_2O)_n](aq) + L(aq) \rightleftarrows [M(H_2O)_{n-1}L](aq) + H_2O$$
$$[M(H_2O)_{n-1}L](aq) + L\ (aq) \rightleftarrows [M(H_2O)_{n-2}L_2](aq) + H_2O$$

and in the general form

$$[M(H_2O)_n](aq) + nL(aq) \rightleftarrows [ML_n](aq) + nH_2O$$

where L = ligand.
Hence, step equilibriums occur [7-9]. If water is disregarded, then

$$K_1 = \frac{[ML]}{[M][L]} \qquad \beta_1 = \frac{[ML]}{[M][L]}$$
$$K_2 = \frac{[ML_2]}{[ML][L]} \qquad \beta_2 = \frac{[ML_2]}{[M][L]^2}$$
$$K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \qquad \beta_n = \frac{[ML_n]}{[M][L]^n}$$

where $K_1, K_2, \ldots, K_n$ = stepwise stability constants;
$\beta_1, \beta_2, \ldots, \beta_n$ = overall stability constants.

It is necessary to know the stability constants of complexes in order to correctly select the most advantageous combinations of reaction conditions and masking agents; this makes it possible to selectively determine chemically similar elements.

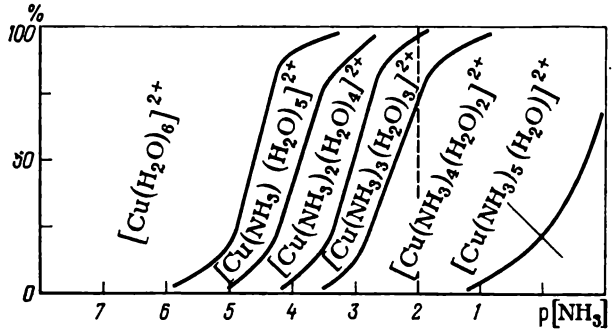


Fig. IX-2. Distribution of complex ions of copper ammoniate

The relative quantity of every type of complex depends on the concentration of the metal and of the ligand. The listeners may be shown a diagram of existence of copper ammoniates in conformity with ammonia concentration (Fig. IX-2) [6] or the regions of existence of the halide complexes of palladium [10].

Experiment 123. Stepwise Dissociation of Bromide Complexes of Copper (II)

Inorganic ligands as a rule link up to the central ion successively and produce a series of complexes with the same ligand that differ from one another by absorption spectra. For example, the absorption bands of the halide complexes of copper that have more than one halide ion are shifted to a longer-wave region:

$$Cu^{2+} + Br^- \rightleftarrows [CuBr]^+ \qquad \log \beta_1 = -0.55 \text{ green}$$

$$[CuBr]^+ + Br^- \rightleftarrows [CuBr_2] \qquad \log \beta_2 = -1.84 \text{ brown}$$

$$[CuBr_2] + 2Br^- \rightleftarrows [CuBr_4]^{2-} \qquad \log \beta_4 = -5.53 \text{ cherry}$$

Reagents

Cupric sulphate, 10 per cent solution.

Hydrobromic acid, 60 per cent solution.

Procedure. Put 100 ml of copper sulphate solution into a cylinder. At the lecture, add hydrobromic acid solution in small portions. The colour changes from blue to green, and then to brown and cherry. A reverse process may be observed by gradually pouring in water.

Note. Colourless hydrobromic acid should be taken for the experiment. In long-standing acid, the bromide ion is oxidized by atmospheric oxygen to element bromine and becomes yellow. It should be kept in a bottle of orange glass and poured into a colourless bottle before a lecture. The acid may be purified by extracting bromine by benzene or carbon tetrachloride.

FACTORS AFFECTING THE STABILITY OF COMPLEXES

The stability of complexes depends on the nature of the metal and of the ligand. The following factors are important in respect to the metal ion: size and charge, ionic potential, energy of stabilization by the crystalline field, and the formation of dative π-bonds.

It is necessary to present a table illustrating the effect of a central ion charge on the stability of complexes (Table IX-4). For comparison, central ions with approximately the same radii (r_i) and the same electron structure have been selected [11].

If the ionic potential is defined as the ratio of the charge of the cation to its radius in a crystal, the stability of complexes with small or high-charge ligands and polydentate ligands increases as the ionic potential grows [6, 12]:

for ions with the same charge, Li > Na > K > Rb > > Cs; Mg > Ca > Sr > Ba > Ra; Al > Sc > Y > La;

for ions with different charges but approximately the same size, Th > Y > Ca > Na; La > Sr > K. However, as we see from Table IX-5, the effect of the metal ion charge on stability is more significant than the effect of the ionic radius [6].

Table IX-4

LOGARITHM OF THE STABILITY CONSTANTS OF COMPLEX IONS IN CONFORMITY WITH THE CENTRAL ION CHARGE

Type of complex ions	log K		
	K^+	Sr^{2+}	La^{3+}
$[M(OH)]^{n-1}$	−0.7	1.0	3.3
$[M(S_2O_3)]^{n-2}$	0.1	2.0	—
	Na^+	Ca^{2+}	Y^{3+} Th^{4+}
$[M(SO_4)]^{n-2}$	0.7	2.3	3.5 4.1
$[M(NO_3)]^{n-1}$		0.3	0.6
$[M(C_2O_4)]^{n-2}$		3.0	7.3
$[MY]^{n-4}$		11.1	18.0
	Ag^+	Hg^{2+}	Tl^{3+}
$[M(OH)]^{n-1}$	2.3	10.3	14.8
$[M(NH_3)]^n$	3.2	8.8	—
$[MCl]^{n-1}$	2.7	5.3	8.1
$[MBr]^{n-1}$	9.0	9.1	9.7

Table IX-5

EFFECT OF THE CHARGE/RADIUS RATIO ON THE STABILITY OF THE $[M(OH)]^{(n-1)+}$ HYDROXOCOMPLEXES

Ion	ionic radius, Å	Charge/radius	log K	Ion	ionic radius, Å	Charge/radius	log K
Li^+	0.78	1.3	0.30	Th^{4+}	1.10	3.6	10.00
Ca^{2+}	1.06	1.9	1.48	Al^{3+}	0.57	5.3	9.00
Ni^{2+}	0.78	2.6	3.48	Be^{2+}	0.34	6.0	7.00
Y^{3+}	1.06	2.8	7.00				

The stability of complexes formed by the ions of transition metals depends not only on the ionic potential, but also on such factors as the energy of stabilization by the crystalline field [6] (Fig. IX-3), the presence of vacant d-orbitals for accepting π-electrons of ligands, and the presence of d-electron pairs for forming dative π-bond.

The stability of complexes for two- and three-charged metals increases in the following order: $d^0 < d^1 < d^2 <$

$< d^3 \geqslant d^4 > d^5 > d^6 < d^7 < d^8 \geqslant d^9 > d^{10}$. In examining the role that a ligand plays in the growth of the stability of complexes, it is important to note the following

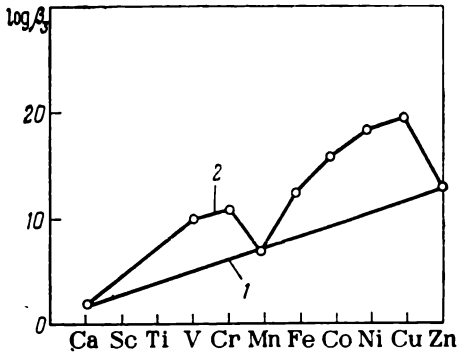


Fig. IX-3. Dependence of the logarithm of the stability constant of complexes of bivalent first-series transition metals with ethylenediamine on the atomic number of a metal:
1 — stabilization by the crystalline field is absent (systems d^0, d^5 and d^{10});
2 — stabilized by the crystalline field (d^1, d^2, d^3, d^4, d^6, d^7, d^8, d^9)

factors (see Chapter X): basicity, ligand dentation, chelate effect, and steric factors.

Experiment 124. Comparative Stability of Chloride Complexes of Zinc and Cobalt

The zinc ion forms more stable complexes with chloride ions than with the cobaltous ion. Although in zinc complex formation there is no stabilization by the ligand field (filled d^{10}-level), the diffuse nature of d-orbitals makes zinc ions easily deformable and promotes the formation of strong covalent complexes with polarizing ligands. Therefore, a zinc ion displaces a cobaltous ion from its chloride complex; the latter is stable in an organic medium:

$$\underset{\text{pale pink}}{2[Co(H_2O)_6]Cl_2} \rightleftarrows \underset{\text{blue}}{Co[CoCl_4]} + 12H_2O$$

$$\underset{\text{blue}}{[CoCl_4]^{2-}} + \underset{}{[Zn(H_2O)_6]^{2+}} \rightleftarrows \underset{\text{colourless}}{[ZnCl_4]^{2-}} + \underset{\text{pink}}{[Co(H_2O)_6]^{2+}}$$

Reagents
Cobaltous chloride, saturated solution.
Zinc chloride.
Acetone.

Procedure. In a cylinder, put 50 ml of cobalt chloride solution. At the lecture, add 100 ml of acetone. Draw the attention of the audience to the fact that the colour of the solution has changed from pink to dark blue. Add 1-2 g of zinc salt and stir. The solution again becomes pink due to the destruction of the cobalt complex.

Experiment 125. Comparative Stability of the Thiocyanate and Fluoride Complexes of Iron

Fluoride complexes of iron (III) are more stable than thiocyanate complexes: $[Fe(NCS)_3]$ $\log \beta_3 = 3.37$; $[FeF_3]$ $\log \beta_3 = 11.86$. This may be demonstrated by using the different colour of complexes:

$$\underset{\text{red}}{[Fe(NCS)_n]^{(3-n)+}} + mF^- \rightleftarrows \underset{\text{colourless}}{[FeF_m]^{(3-m)+}} + nNCS^-$$

Reagents
Ferric chloride, 1 per cent solution in 0.1 *N* hydrochloric acid solution.
Ammonium thiocyanate, 10 per cent solution.
Ammonium fluoride, 20 per cent solution.
Sulphuric acid, 0.5 *M* solution.

Procedure. In a cylinder, put 5 ml of ferric chloride solution, 200 ml of water and 20 ml of sulphuric acid. At the lecture, add 50 ml of ammonium thiocyanate solution. An intense red colour appears. Add 50 ml of ammonium fluoride solution. The colour disappears.

Experiment 126. Effect of Outer-sphere Anion on the Stability of the Copper-Benzidine Complex

The cupric ion forms with benzidine the red-brown complex $[CuBzd]^{2+}$. The complex is not decomposed in the presence of chloride ions and sulphate ions; it is decomposed

in the presence of bromide ions and iodide ions. At that, benzidine is oxidized by cupric ions with the formation of benzidine blue. $E^{f}_{\text{Bzd (violet)/Bzd (colourless)}} = 0.69\,\text{V}$, $E^{\circ}_{Cu^{2+}/Cu^{+}} = 0.153\,\text{V}$, $E^{\circ}_{Cu^{2+}/CuI} = 0.86\,\text{V}$.

Reagents
Cupric sulphate, 1 per cent solution.
Benzidine, 0.1 per cent ethanol solution.
Potassium iodide, 5 per cent solution.

Procedure. On a strip of filter paper, deposit a drop of copper sulphate solution and a drop of benzidine solution; a red-brown copper-benzidine complex is formed. Deposit a drop of potassium iodide solution; a dark blue spot or ring is observed.

Experiment 127. Comparative Stability of the Benzidine and Tolidine Complexes of Copper

Like benzidine, tolidine forms with the cupric ion the brown-red complex compound $[CuTol]^{2+}$. This complex is less stable than $[CuBzd]^{2+}$, and it is decomposed in the presence of not only bromide ions and iodide ions, but also chloride ions with the formation of tolidine blue.

Reagents
Cupric sulphate, 1 per cent solution.
Potassium chloride, 5 per cent solution.
Benzidine, 0.1 per cent ethanol solution.
Tolidine, 0.01 per cent ethanol solution.

Procedure. On a strip of filter paper, deposit a drop of copper sulphate solution, a drop of tolidine solution and a drop of potassium chloride solution. A dark blue spot or ring is formed. On another strip of filter paper, deposit a drop of copper sulphate solution, a drop of benzidine solution and a drop of potassium chloride solution. The formation of a red-brown copper-benzidine complex is observed.

INERT AND LABILE COMPLEXES

Inert complexes are compounds in which ligand exchange occurs at a measurable rate; in labile complexes, replacement is instantaneous. It is important to note that these two expressions, i.e., inert and labile complexes, relate to reaction rates, and they should not be confused

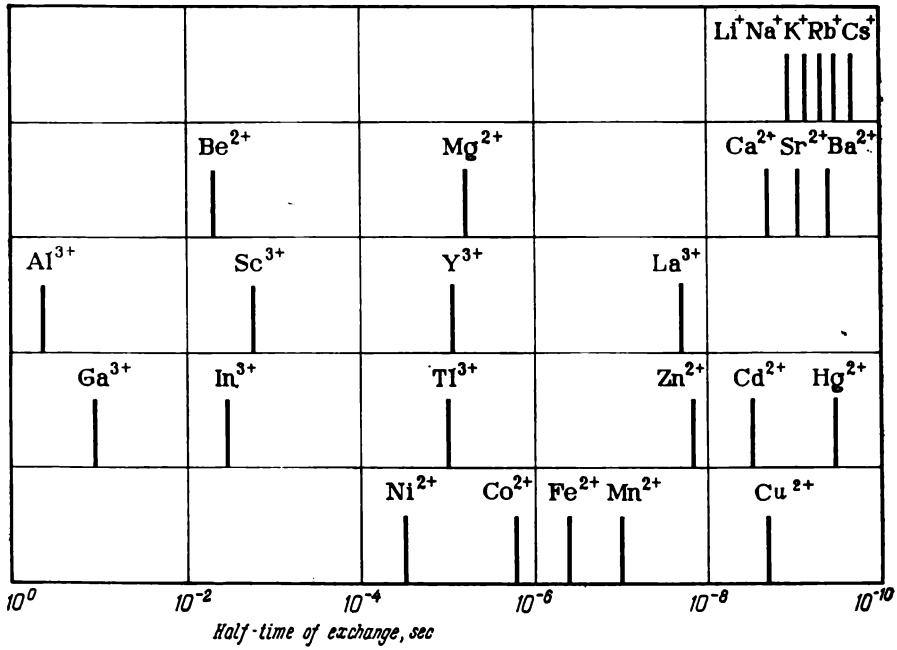


Fig. IX-4. Exchange rate of water molecules in the internal coordination sphere of aquo complexes of metals

with the expression "stable and unstable complexes", which determines the thermodynamic tendency of existence under equilibrium conditions. Most metal ions form labile complexes. There are only a few inert complexes, and they are mainly complexes of some transition metals. The listeners may be shown a diagram of the exchange rate of water molecules in the inner coordination sphere of aquo complexes of metals (Fig. IX-4) [6, 13].

Experiment 128. Comparative Kinetic Stability of the Aquo Complexes of Iron (III) and Chromium (III)

The aquo complexes $[Fe(H_2O)_6]^{3+}$ and $[Cr(H_2O)_6]^{3+}$ have almost the same binding energy, it being 485 kJ/mol and 510 kJ/mol, respectively, and consequently they have practically the same stability. However, the aquo complex of iron (III) is labile, and the aquo complex of chromium (III) is inert (see Experiment 32); therefore, the reaction of iron (III) with EDTA proceeds very rapidly, while there is virtually no reaction with chromium (III). The difference in the kinetic stability of the aquo complexes of iron and of chromium is used for their separate determination.

Reagents

Ferric chloride, 1 per cent solution in 1 *M* hydrochloric acid solution.
Chromic chloride, 1 per cent solution in 0.1 *N* hydrochloric acid solution.
EDTA, 0.1 *M* solution.
Acetic acid, 2 *M* solution.

Procedure. In a 500-ml beaker, put 20 ml of ferric chloride solution and 300 ml of water. In another heat-resistant beaker, put 20 ml of chromium chloride solution, 30 ml of acetic acid solution and 300 ml of water. To each beaker, add 50 ml of EDTA solution. The yellow colour of the iron complex immediately appears in the first beaker; no changes are observed in the second one. Heat the solution in the second beaker with a burner. The crimson-violet colour of the chromic complex appears.

MIXED COMPLEXES

Complexes with a mixed coordination sphere are the most probable form of existence of ions in solutions. They have a more intense colour (see Experiment 10), higher stability and are extracted better into organic solvents [14] than simple complexes.

There are also mixed complex compounds which contain different metals (multinuclear complexes).

Experiment 129. Complex of Copper (II) with Pyridine and Salicylate Ions

The cupric ion forms with salicylate ions the green complex $[Cu(Sal)_2]^{2-}$ ($\log \beta_2 = 18.4$, 20° C, $\mu = 0.1$) and with pyridine the dark blue complex $[CuPy_4]^{2+}$ ($\log \beta_1 = 6.54$, 25° C, $\mu = 1$). Both compounds are insoluble in chloroform. When both complexes are mixed together, different types of mixed compounds are formed in conformity with the pH and other conditions, $[CuPy_2Sal]$, $[CuPy_2(HSal)_2]$ and $[PyH]_2[Cu(Sal)_2]$, which are more intensely coloured and soluble in chloroform.

Reagents

Cupric sulphate, 1 per cent solution.
Salicylic acid, saturated solution.
Pyridine.
Chloroform.

Procedure. Take two cylinders and in each of them put 5 ml of copper sulphate solution and 100 mi of water. At the lecture, add 50 ml of salicylic acid solution to one cylinder; a green complex is formed. Add 20 ml of pyridine to the other one; a dark blue compound is formed. To each cylinder, add 50 ml of chloroform and shake (use a protective screen!). The chloroform layer remains colourless. Mix the contents of both cylinders and shake. The chloroform layer becomes dark blue.

Experiment 130. Binuclear Compound of Scandium and Yttrium with Lumogallion

Chelates of scandium and yttrium with lumogallion are poorly extracted with ethers. A mixed binuclear compound is highly soluble in diethyl ether (pH = 4-5). The complex-formation reaction may be presented in the following manner [15]:

$$[MOH]^{2+} + H_2R \rightleftarrows [RMOH] + 2H^+$$

$$M_1^{3+} + H_2R \rightleftarrows [M_1R]^+ + 2H^+$$

$$[RMOH] + [M_1R]^+ \rightleftarrows [RM{-}O{-}M_1R] + H^+$$

where H_2R = lumogallion.

The reaction of formation of the mixed complex has higher sensitivity: the apparent molar absorption coefficient ($\bar{\varepsilon}$) of the ScYR compound is $3.4 \cdot 10^4$ at $\lambda = 480$ nm, while that of the ScR compound is $1.0 \cdot 10^4$.

Reagents

Scandium trichloride, 0.01 *M* solution in 0.01 *N* hydrochloric acid solution.

Yttrium trichloride, 0.01 *M* solution in 0.01 *N* hydrochloric acid solution.

Diethyl ether.

Lumogallion, 0.01 per cent solution.

Procedure. In one cylinder, put 5 ml of scandium chloride solution, and in the other, 5 ml of yttrium chloride solution. To each cylinder, add 100 ml of water and 20 ml of lumogallion solution. The appearance of a pink colour is observed. To each cylinder, add 50 ml of diethyl ether and shake (use a protective screen!). The organic layer remains almost colourless. Mix the contents of both cylinders together and shake. The layer of diethyl ether becomes red, and the aqueous phase is colourless.

STABILIZATION OF UNSTABLE DEGREES OF OXIDATION OF ELEMENTS BY COMPLEX FORMATION

To stabilize the unstable degrees of oxidation of elements, such as Co^{3+}, Cu^{3+}, Pb^{4+} and Mn^{3+}, complex formation is performed with different ligands. Hence, the high redox potential of the pairs Cu^{3+}/Cu^{2+}, Pb^{4+}/Pb^{2+} and Mn^{3+}/Mn^{2+} determines their high reactivity in aqueous solutions. Complex formation reduces the potential and makes it possible for these compounds to exist in solution:

Unstable	Stable
Cu^{3+}	$[Cu(ClO_4)_4]^-$, $[Cu(IO_6)_2]^{7-}$
Pb^{4+}	$[PbCl_6]^{2-}$
Mn^{3+}	$[Mn(H_2P_2O_7)]^+$
Co^{3+}	$[Co(NO_2)_6]^{3-}$

Using different oxidizing and reducing agents, many complexes may be produced in the presence of ligands; in these complexes, the central metal ion has an unusually low or high degree of oxidation.

The effect of complex formation on the redox potential of ions may be shown by Experiments 99-102.

The redox potential of metal ions noticeably changes when the type of ligand changes; this may lead to the stabilization of the highest degrees of oxidation (the values of E^0 in volts are given in parentheses) [6]:

	E°
$[Fe(H_2O)_6]^{3+} + \bar{e} \rightleftarrows [Fe(H_2O)_6]^{2+}$	(0.77)
$[Fe(CN)_6]^{3-} + \bar{e} \rightleftarrows [Fe(CN)_6]^{4-}$	(0.36)
$[FeY]^- + \bar{e} \rightleftarrows [FeY]^{2-}$	(−0.12)
$[Co(H_2O)_6]^{3+} + \bar{e} \rightleftarrows [Co(H_2O)_6]^{2+}$	(1.84)
$[Co(NH_3)_6]^{3+} + \bar{e} \rightleftarrows [Co(NH_3)_6]^{2+}$	(0.10)

Experiment 131. Stabilization of the Manganic Ion by Complex Formation

The manganic ion is a very strong oxidizing agent, $E^\circ_{Mn^{III}/Mn^{II}} = 1.6$ V. If the manganic ion is not stabilized by complex formation, the reaction proceeds spontaneously

$$2Mn^{3+} + 2H_2O \rightleftarrows MnO_2 + Mn^{2+} + 4H^+$$

This restricts the utilization of manganese (III) as a reagent. Fluoride ions, pyrophosphate ions, sulphate ions and ethylenediaminetetraacetic acid are used as ligands. In the presence of pyrophosphate ions, the potential of half-reaction decreases to approximately 1.15 V, and in the presence of sulphate ions (8 *M* H_2SO_4), to 1.48 V.

Reagents

Manganous chloride, 5 per cent solution.
Hydrogen peroxide, 3 per cent solution.
EDTA, saturated solution.
Sodium hydroxide, 0.1 *N* solution.

Procedure. In a cylinder, put 100 ml of manganese chloride solution. At the lecture, add an equal amount of EDTA solution, 5 ml of hydrogen peroxide solution and

20 ml of sodium hydroxide solution, and stir. The solution assumes the red-violet colour of the manganic complexonate.

Experiment 132. Reaction of Oxidation of the Complex of Cobalt with EDTA

The reaction of oxidation of cobalt ethylenediaminetetraacetate by potassium ferricyanide occurs according to the following pattern

$$\underset{\text{pale pink}}{[CoY]^{2-}} + [Fe(CN)_6]^{3-} \rightleftarrows \underset{\text{violet}}{[CoY]^{-}} + [Fe(CN)_6]^{4-}$$

In the reaction of $[CoY]^{2-}$ with bromine, cobalt directly reacts with bromine and the latter is reduced [6]:

$$\underset{\text{pale pink}}{[CoY]^{2-}} + Br_2 \rightleftarrows [CoY \ldots Br_2]^{2-} \rightleftarrows Br + \underset{\text{pink}}{[CoYBr]^{2-}}$$

Reagents

Cobaltous chloride, 1 per cent solution.
EDTA, 0.1 *M* solution.
Potassium ferricyanide, 1 per cent solution.
Bromine, saturated solution.

Procedure. In a cylinder, put 20 ml of cobalt chloride solution and 300 ml of water. At the lecture, divide the solution into two parts and add 50 ml of EDTA solution to each of them. To one part, add 5 ml of potassium ferricyanide solution; the formation of the violet cobalt complex is observed. To the other part, add 5 ml of bromine water; the colour becomes pink.

INCREASE IN THE IONIZATION CONSTANT OF A WEAK ELECTROLYTE AS A RESULT OF COMPLEX FORMATION

Experiment 133. Reaction Between Boric Acid and Polyatomic Alcohols

Boric acid is a weak monobasic acid ($pK_a = 9.28$, 20° C, $\mu \to 0$); therefore, its solutions cannot be titrated with alkaline solutions. However, in the presence of polyoxy com-

pounds (glycerol, mannitol, glucose) borate anions are stabilized due to the formation of chelates in which some or all water molecules surrounding a borate ion are replaced by hydroxy groups of organic ligands. This stabilization increases the strength of boric acid so greatly that it may be titrated with alkali in the presence of phenolphthalein [16]. The ionization constants of complex acids of boron with polyoxy compounds are given below:

	pK_a
Ethylene glycol, boric	8.25
Glycerol, boric	6.98
Glucose, boric	6.39
Fructose, boric	5.31
Sorbitol, boric	4.81

Complexes may be formed in which the borate-ligand ratio is 1 : 1 and 1 : 2. For example, for a complex with mannitol:

$$2CH_2OH(CHOH)_4CH_2OH + H_3BO_3 \rightleftarrows H\{BO_2[C_6H_8(OH)_6]_2\} + H_2O$$

$$HA \rightleftarrows H^+ + A^- \qquad pK_1 = 9.19$$

$$M + A^- \rightleftarrows MA^- \qquad \log \beta_1 = 2.48$$

$$M + MA^- \rightleftarrows M_2A^- \qquad \log \beta_2 = 2.23$$

where M = mannitol;
HA = boric acid.

On the whole, $HA + 2M \rightleftarrows H^+ + M_2A^-$ and $pK = p(K_1 \cdot \beta_1 \cdot \beta_2) = 4.48$.

A change in acid properties may be demonstrated by using the congo red indicator (pH range 3.0-5.2), which is red at pH > 5.2 and dark blue-violet at pH < 3. The pH-value of 0.1 *N* boric acid solution is approximately 5.2, and that of 0.1 *N* mannitol-boric acid solution, 2.75.

Similarly, the acid properties of germanic acid, H_2GeO_3, may be intensified, and the titrimetric determination of germanium ($pK_a = 9.05$) may be effected.

Reagents

Boric acid, 0.1 *N* solution.
Glycerol or mannitol.
Congo red, 0.1 per cent solution.

Procedure. In a cylinder, put 500 ml of boric acid solution and 10 ml of congo red. The solution is pink. At the lecture, divide the solution into two parts. Keep one part for reference. To the other part, add 100 ml of glycerol or 5-10 g of mannitol and stir. The solution becomes dark blue-violet.

MASKING AND DEMASKING

Masking is a method of eliminating the interfering influence of ions, when the ion being masked loses, under the influence of the masking reagent, the ability to produce some of its characteristic reactions [17, 18]. In masking, there is a decrease in the apparent constant of the reaction in which the ion being masked participates.

Experiment 134. Masking of the Ferric Ion by Fluoride Ions in Detecting the Cobaltous Ion

The ability of ferric ions to form strong complexes with fluoride ions is used in analysis for masking iron (III) and in detecting and photometrically determining some ions, such as cobalt ions and nickel ions (see Experiments 36, 38, 125)

$$Fe^{3+} + nNCS^- \rightleftarrows \underset{\text{red}}{[Fe(NCS)_n]^{(3-n)+}}$$

$$Co^{2+} + mNCS^- \rightleftarrows \underset{\text{dark blue}}{[Co(NCS)_m]^{(2-m)+}}$$

$$[Fe(NCS)_n]^{(3-n)+} + pF^- \rightleftarrows nNCS^- + \underset{\text{colourless}}{[FeF_p]^{(3-p)+}}$$

$\log \beta_3 = 3.57$ (18 °C, $\mu = 1.8$) $\log \beta_3 = 11.86$ (25 °C, $\mu = 0.5$)

Reagents

Ferric chloride, 1 per cent solution in 0.1 *N* hydrochloric acid solution.
Cobaltous chloride, 1 per cent solution.
Ammonium thiocyanate, 10 per cent solution.
Ammonium fluoride, 20 per cent solution.

Acetone.
Hydrochloric acid, concentrated.

Procedure. In a cylinder, put 1 ml of iron chloride solution, 5 ml of cobalt chloride solution, 20 ml of water, 5 ml of hydrochloric acid and 250 ml of acetone. At the lecture, add 50 ml of ammonium thiocyanate solution. A mixed dark brown colour of the complexes of iron and cobalt is observed. Divide the mixture into two parts. To one part, add 50 ml of ammonium fluoride solution. The blue colour of a cobalt thiocyanate complex appears.

Experiment 135. Masking and Demasking of the Titanium Ion

Titanium (IV) ions form with hydrogen peroxide yellow complexes which exist in the range of hydrogen ion concentration from pH 0.3 to 6 *M*.

It is impossible to determine the titanium (IV) ion by hydrogen peroxide in the presence of fluoride ions due to the masking of titanium ions with the formation of the complexes $[TiF_6]^{2-}$ and $[TiOF_4]^{2-}$. Aluminium ions bind fluoride ions into complex ions, thus demasking titanium (IV) ions.

In literature, views differ as to the structure of complexes. One of the possible arrangements of the formation and decomposition of complexes may be:

$$TiO^{2+} + H_2O_2 + SO_4^{2-} \rightleftarrows [TiO(H_2O_2)SO_4]$$

$$2[TiO(H_2O_2)SO_4] + nF^- \rightleftarrows [TiOF_{n-1}]^{(3-n)+} + \\ + [TiO(H_2O_2)F]^+ + H_2O_2 + 2SO_4^{2-}$$

$[AlF_n]^{(3-n)+}$ $\log K_1 = 6.13$; $\log K_2 = 5.05$; $\log K_3 = 3.91$; $\log K_4 = 2.71$; $\log K_5 = 1.46$; $\log K_6 = 0.47$ (25 °C $\mu = 0.5$)

$[TiOF_n]^{(2-n)+}$ $\log K_1 \approx 5.38$; $\log K_2 = 4.35$; $\log K_3 = 3.96$; $\log K_4 = 3.72$ (25 °C, $\mu = 3$)

As demasking ions, use may be made of also zirconium (IV) ions, which form the complex $[ZrF_6]^{2-}$ ($\log \beta_6 = 34.4$, 25° C, $\mu = 0.5$), or borate ions which form with fluoride ions colourless complexes:

$$H_3BO_3 + 3H^+ + 4F^- \rightleftarrows [BF_4]^- + 3H_2O \quad \log K = 20.0$$
(25 °C, $\mu = 0$).

It should be noted that the fading of colour as a result of the destruction of the complex of titanium with hydrogen peroxide, and also of the complex of iron with thiocyanate ions under the action of fluoride ions, is used for quantitatively determining fluoride ions.

Reagents

Aluminium trichloride, solution containing 10 mg/ml of aluminium.
Titanium (IV) sulphate, solution in 9 *M* sulphuric acid solution containing 1 mg/ml of titanium.
Ammonium fluoride, 10 per cent solution.
Hydrogen peroxide, 3 per cent solution.
Sulphuric acid, 2 *M* solution.

Procedure. In a cylinder, put 10 ml of titanium sulphate solution, 150 ml of sulphuric acid solution and 150 ml of water. At the lecture, add 20 ml of hydrogen peroxide solution. The formation of yellow peroxotitanyl ions is observed. Add an ammonium fluoride solution until the solution becomes colourless. Divide the solution into two parts. Keep one part for reference. To the other part, add 50 ml of aluminium chloride solution. The yellow colour of peroxotitanyl ions reappears.

Experiment 136. Masking and Demasking of the Ferric Ion

The ferric ion is masked by fluoride ions (see Experiment 134). The ferric ion may be demasked by introducing aluminium ions or borate ions, which form stronger complexes with fluoride ions.

Reagents

Ferric chloride, 0.01 per cent solution in 0.1 *N* hydrochloric acid solution.
Aluminium chloride, solution containing 10 mg/ml of aluminium in 0.01 *N* hydrochloric acid solution.
Ammonium thiocyanate, 10 per cent solution.
Ammonium fluoride, 10 per cent solution.

Procedure. In a cylinder, put 25 ml of ferric chloride solution and 300 ml of water. At the lecture, add 30 ml of ammonium thiocyanate solution. Red iron thiocyanate is

formed. Add ammonium fluoride solution until the red colour disappears. Divide the solution into two parts. Keep one part for reference. To the other, add 50 ml of aluminium chloride solution and stir. The red colour of iron thiocyanate reappears.

EFFECT OF TEMPERATURE ON COMPLEX FORMATION

On heating, intramolecular interactions are intensified in molecules which have a relatively large reserve of vibrational and rotational energy. This intensifies the colour of some complexes [19].

Experiment 137. Reaction Between the Ferric Ion and Sulphosalicylic Acid on Heating

The ferric ion forms with sulphosalicylic acid in an acid medium a violet-pink complex at room temperature (see Experiment 40). On heating to 80° C, the colour of the complex intensifies to bright violet [20].

Reagents

Ferric chloride, 0.1 per cent solution in 0.1 *N* hydrochloric acid solution.
Sulphosalicylic acid, 10 per cent solution.
Sulphuric acid, 1 *M* solution.

Procedure. In a heat-resistant glass beaker, put 2 ml of ferric chloride solution, 20 ml of sulphuric acid solution and 300 ml of water. At the lecture, add 50 ml of sulphosalicylic acid solution. A violet-pink complex is formed. Heat the solution with a burner. The intensification of colour is observed.

Experiment 138. Reaction Between the Phosphate Ion and Molybdate Ion on Heating

The phosphate ion forms with the molybdate ion, in an acid medium (0.7 *N* sulphuric acid), a molybdophosphoric acid of yellow colour $H_3[PMo_{12}O_{40}]$. On heating, the colour intensifies [21].

Reagents

Potassium dihydrophosphate, 0.1 per cent solution.
Sodium molybdate, 10 per cent solution.
Sulphuric acid, 0.5 *M* solution.

Procedure. In a heat-resistant glass beaker, put 20 ml of potassium dihydrophosphate solution, 50 ml of sulphuric acid solution and 200 ml of water. At the lecture, add 40-50 ml of sodium molybdate solution. The complex becomes yellow. Heat the solution with a burner. The colour becomes more pronounced.

PRECIPITATION OF COMPLEXES

The hydration energy of large ions is not great; therefore, such cations or cationic complexes are precipitated in the presence of large anions or anionic complexes. The solubility of complex salts is determined by the totality of the following factors: the ratio of the radii of ions which constitute a given salt should approximate a certain value (0.7-1.2); when the charge of the complex ion increases, solubility decreases. The presence of groups which are capable of forming hydrogen bonds with water molecules leads to an increase in the solubility, and the polarity leads to a decrease in the solubility of the complex [22].

As large cations, use is made of the cations Cs, Rb, Tl and others (Table VI-10), and also of the cations of such bases as the amino derivatives of the triphenylmethane series, alkaloids and heterocyclic N-derivatives, and as large anions, use is made of the halide complexes of cadmium, mercury (II), bismuth (III) and other metals, perrhenate, tungstate, and so forth.

Experiment 139. Precipitation of the Iodide Bismuth Complex by Cinchonine

The bismuthous ion in weak-acid solutions forms several complex ions in the presence of iodide ions. The complex anions $[BiI_4]^-$ and $[BiI_6]^{3-}$ ($\log \beta_6 = 19.4$, 20° C, $\mu = 3$)

exist in an excess of iodide ions (see Experiment 59):

$$Bi^{3+} \overset{I^-}{\rightleftarrows} [BiI]^{2+} \overset{I^-}{\rightleftarrows} [BiI_2]^{+} \overset{I^-}{\rightleftarrows} \underset{\text{black precipitate}}{BiI_3} \overset{I^-}{\rightleftarrows} \underset{\text{yellow solution}}{[BiI_4]^-}$$

$$\log \beta_1 = 3.63 \ (25^\circ C, \ \mu \approx 0.5); \quad -\log K_{sp} = 18.09; \quad \log \beta_4 = 14.95 \ (20^\circ C, \ \mu \approx 3)$$

The $[BiI_4]^-$ ion is precipitated by large molecules of alkaloids (cinchonine, strychnine) in the form of an orange-red precipitate, such as the ion associate $[RH^+][BiI_4^-]$, where R is an alkaloid molecule.

Reagents

Bismuthous nitrate, 1 per cent solution in 1 *M* nitric acid solution.

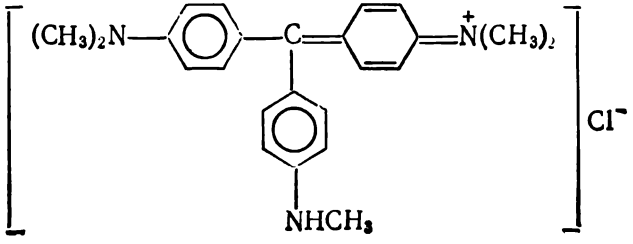
Potassium iodide, 10 per cent solution.

Cinchonine.

Procedure. In a cylinder, put 10 ml of bismuth nitrate solution and 250 ml of water. At the lecture, add potassium iodide solution until the bismuth iodide precipitate completely dissolves. Draw the attention of the audience to the formation of a complex bismuthous anion. To the dark yellow solution of the bismuth iodide complex, add 20-30 mg of cinchonine (on the end of a spatula) and stir. The formation of a bulky orange precipitate is observed.

Experiment 140. Reaction Between the Zinc Thiocyanate Complex with Methyl Violet

In aqueous solutions, methyl violet forms a stable cation:



Amino groups in triphenylmethane dyes are determinative in the stability of the cation and in its absorbance.

In acid solutions, amino groups are protonated and the colour gradually changes from violet to blue and then to yellow, depending on the number of bound hydrogen ions.

With thiocyanate complexes, such as those of zinc or copper, the cation of the dye forms slightly soluble compounds of a dark blue colour:

$$Zn^{2+} \overset{NCS^-}{\rightleftharpoons} [Zn(NCS)]^+ \overset{NCS^-}{\rightleftharpoons} [Zn(NCS)_2] \overset{NCS^-}{\rightleftharpoons}$$
$$\log \beta_1 = 1.57 \qquad \log \beta_2 = 1.56$$

$$\rightleftharpoons [Zn(NCS)_3]^- \overset{NCS^-}{\rightleftharpoons} [Zn(NCS)_4]^{2-}$$
$$\log \beta_3 = 1.51 \qquad \log \beta_4 = 3.02\ (\mu \to 0)$$

Reagents

Zinc chloride, 2 per cent solution.
Methyl violet, 0.05 per cent solution.
Ammonium thiocyanate, 20 per cent solution.
Hydrochloric acid, 2 *M* solution.

Procedure. In a cylinder, put 100 ml of zinc chloride solution, 100 ml of water and 10 ml of hydrochloric acid. At the lecture, add 20 ml of methyl violet solution. The solution becomes blue, which is characteristic of the protonated ions of the dye. Divide the solution into two parts. Keep one part for reference; to the other part, add 50 ml of ammonium thiocyanate solution and stir. A dark blue suspension appears.

Note. The precipitation of cationic complexes by large anions may also be demonstrated, such as the precipitation of the iron (III) 1,10-phenanthroline complex by perchlorate ions. See also Experiment 94.

SOLVENT EXTRACTION OF METAL COMPLEXES

An important property of complexes that is used in analysis and likewise in the study of the structure and of the quantitative characteristics of complexes is their ability to be extracted by many organic solvents [23, 24]. In expounding this section, use may be made of experiments in which

extraction is employed for the purpose of increasing the sensitivity and selectivity of the reactions of complex formation (Experiments 6, 7), and also experiments in the extraction of complexes of metals with organic ligands (Experiments 164-168).

Experiment 141. Extraction of Iron (III) Complexes from Hydrohalic Acid Solutions

Extraction from hydrohalic acid solutions may occur via three mechanisms [25]: extraction of molecular compounds without chemical interactions in the organic phase (physical distribution), the solvate mechanism (comparatively strong chemical interaction) and the hydrate-solvate mechanism. Extraction reactions may be written in the general form by the following equations:

$$MX_{q\,aq} \overset{K_{ph}}{\rightleftarrows} MX_{q\,org} \quad \text{(physical distribution)}$$

$$MX_q(H_2O)_{p\,aq} + nS_{org} \overset{K_s}{\rightleftarrows} MX_q(H_2O)_pS_{n\,org}$$

(solvate mechanism)

$$iH^+_{aq} + [MX_q(H_2O)\,p]^{i-}_{aq} + mH_2O_{aq} + nS_{org} \overset{K_{h.\,s}}{\rightleftarrows}$$

(hydrate-solvate mechanism)

$$\rightleftarrows [H_i(H_2O)_mS_n][MX_q(H_2O)_p]_{org}$$

where

K = corresponding constants;
q, p, i, m, n = stoichiometric coefficients;
X = halide ion;
S = solvent.

For example, the extraction of chlorides of arsenic $AsCl_3$ and germanium $GeCl_4$ may be regarded as physical distribution. Strong-base extractants (tributyl phosphate and similar solvents) extract many compounds via the solvate mechanism. In concentrated solutions of hydrochloric and hydrobromic acids, ferric hexaquo ions form ions $[FeX_4]^-$, and metal halo acids are extracted by oxygen-bearing sol-

vents via the hydrate-solvate mechanism. The main cause of extraction of metal halo acids is the solvation of a hydrated proton (or a hydroxonium ion, to be more exact) which then combines with an anion, and the associate formed is transferred to the organic phase.

Reagents

Ferric chloride, 1 per cent solution in 0.1 *N* hydrochloric acid solution.
Hydrobromic acid, concentrated.
Diethyl ether.

Procedure. In a cylinder, put 2 ml of ferric chloride solution and 100 ml of water. At the lecture, add 100 ml of hydrobromic acid. The acid $H[FeBr_4]$ of a dark yellow colour is formed. Add 100 ml of diethyl ether and shake (use a protective screen!). Observe the phase separation against a white screen. The organic phase has a dark yellow colour, and the aqueous phase is colourless.

Note. For demonstration, use may be made of Experiment 6 and also of the extraction of $H[FeCl_4]$ from a hydrochloric acid solution. However, the extraction of $H[FeBr_4]$ is more illustrative, since this complex compound has an intense colour.

COMPLEXONES IN CHEMICAL ANALYSIS

In the general course in analytical chemistry, a special lecture is devoted to complexones, since they are widely used in modern analytical methods [26]. Mendeleyev's table given below shows the elements which are determined by the complexonometric method.

Complexones are derivatives of α-amino acids or of aliphatic and aromatic diamines which contain one or more methyl carboxyl groups [26, 27]. Lecture experiments are carried out with ethylenediaminetetraacetic acid (complexone II) or its disodium salt (EDTA, complexone III).

At the lecture, it is expedient to show a diagram of the distribution of different forms of EDTA as dependent on the pH (Fig. IX-5), drawing particular attention to the region of existence of the ethylenediaminetetraacetate ion Y^{4-} (pH = 8-12), and to present the values of the conse-

I	II	III	IV	V	VI	VII	VIII		I	II	III	IV	V	VI	VII	O
H																He
Li	Be										B	C	N	O	F	Ne
Na	Mg										Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac**	Ku														

*Lanthanoids

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

**Actinoids

Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	(No)	Lr

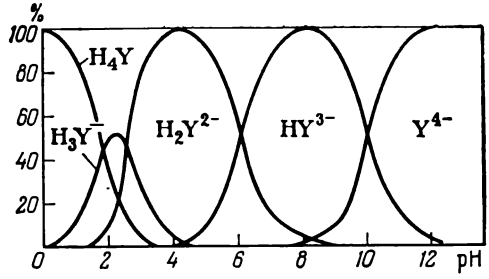


Fig. IX-5. Diagram of the state of ethylenediaminetetraacetate ions as dependent on the pH

cutive constants of ionization of different forms, which are given below ($\mu = 0.1$, 20° C):

$$H_6Y^{2+} \rightleftarrows H_4Y + 2H^+ \quad pK_0 = 1.72$$

$$H_4Y \rightleftarrows H_3Y^- + H^+ \quad pK_1 = 2.00$$

$$H_3Y^- \rightleftarrows H_2Y^{2-} + H^+ \quad pK_2 = 2.67$$

$$H_2Y^{2-} \rightleftarrows HY^{3-} + H^+ \quad pK_3 = 6.16$$

$$HY^{3-} \rightleftarrows Y^{4-} + H^+ \quad pK_4 = 10.26$$

In presenting the general arrangement of complex formation, attention should be drawn to the varied dentation of the reagent that is due to the nature of the complexing element. In addition, illustrations may be used to show the spatial distribution of atoms in the complexes of cobalt (dentation is 6) and nickel (dentation is 5, Fig. IX-6). It is important to note that in the complexes, the stoichiometric ratio of the components is 1 : 1 with the exception

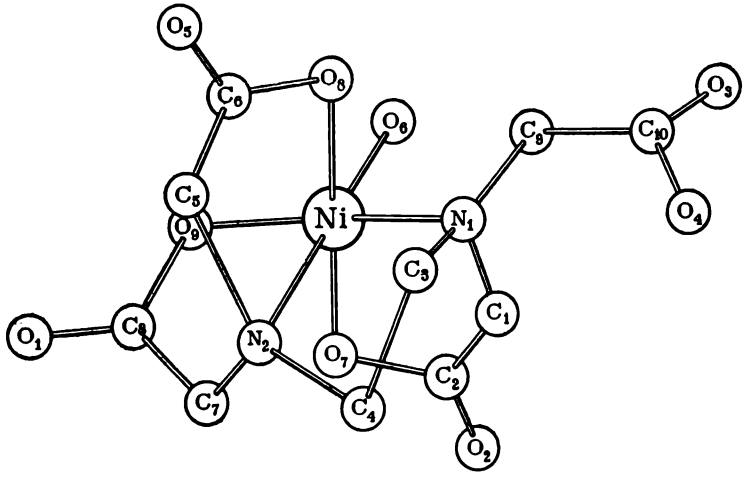


Fig. IX-6. Spatial distribution of atoms in the nickel complexonate

of the complexes of molybdenum (V, VI) and tungsten (V) in spite of the diverse forms of the complexonates, depending on acidity (protonated, ordinary, hydroxo, mixed complexes).

Utilization of EDTA for Ion Detection

Experiment 142. Coloured Complexes of Metals with EDTA

In detecting some ions (elements with *d*-configurations), their power to form coloured complexonates may be used. At pH = 1.5 ÷ 4, the chromic ion forms, when heated to 80° C, the crimson-violet compound $[CrY]^-$, and at pH = = 8 ÷ 10, the lilac hydroxocomplexonate $[Cr(OH)Y]^{2-}$;

a ferric complexonate has a yellow colour, and in the presence of hydrogen peroxide, a mixed complex of red colour is formed. The manganous complexonate is pale pink, and the manganic complexonate is red-violet. Cobaltous, cobaltic, nickelous and cupric complexonates are also coloured.

Reagents

Ferric, nickelous, cobaltous and cupric chlorides, 1 per cent solutions.
EDTA, saturated solution.
Hydrogen peroxide, 30 per cent solution.
Sodium hydroxide, 2 *M* solution.

Procedure. Take several cylinders and in each of them put 100 ml of metal chloride solutions. At the lecture, add 100 ml of EDTA solution to each cylinder. The yellow colour of the iron (III) complex, the blue colour of a copper and nickel complex, and the pink colour of the cobalt complex appear. Divide the iron complex solution into two parts. Keep one part for reference. To the other part, add 20 ml of hydrogen peroxide solution and 5 ml of alkaline solution. The colour changes to bright red.

Note. The experiment may be carried out beforehand, and the cylinders with the appropriate labels may be put on the demonstration table. In this case, the chromic complex may also be prepared (see Experiment 128).

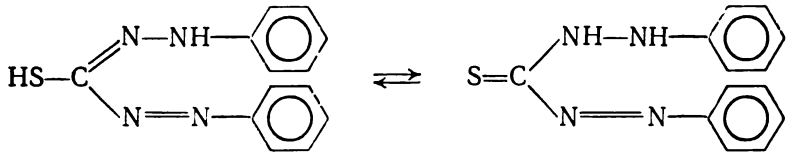
Masking with EDTA

Many ions form strong ethylenediaminetetraacetates, and at some pH values these complexes are so stable that the ions forming them do not enter into many analytical reactions. Apart from the pH, masking is considerably affected also by the reagent concentration, temperature, the reaction rate, and so forth [17, 28].

Experiment 143. Masking of Zinc Ions with EDTA

Dithizone reacts with many transition metals which have filled *d*-orbitals. In this case, intensely coloured complexes in which metal is bound to nitrogen and the thio

group are formed:



thiolate form dithizone thionate form

The mercuric ion forms a strong orange complex, which is extracted by chloroform and carbon tetrachloride. The zinc ion forms a red chelate. In an acetate buffer solution (pH = 5), zinc is bound into a more stable complex with EDTA; the mercuric dithizone is stable under these conditions:

$$\left.\begin{array}{ll}[HgY]^{2-} & \log \beta_1 = 21.8 \\ [ZnY]^{2-} & \log \beta_1 = 16.4\end{array}\right\} (25\,^{\circ}C,\ \mu = 0.1)$$

$$Hg^{2+} + 2HL^{-} \rightleftarrows Hg(HL)_2 \quad \log \beta_2 = 40.34 \ (25\,^{\circ}C,\ \mu = 0)$$

where H_2L = dithizone.

This is used in photometric analysis for determining zinc in the presence of mercury.

Reagents

Zinc chloride, 0.1 per cent solution.

Mercuric nitrate, 0.1 per cent solution in 0.1 *N* nitric acid solution.

Dithizone, 0.01 per cent solution in carbon tetrachloride.

EDTA saturated solution.

Acetate buffer solution (pH = 5). Equal amounts of 2 *M* solutions of acetic acid and sodium acetate are mixed together.

Procedure. In a cylinder, put 10 ml of zinc chloride solution, and in the other, 10 ml of mercury nitrate solution. Into each cylinder, pour 100 ml of water and 50 ml of acetate buffer solution. At the lecture, add 100 ml of dithizone solution to each cylinder and shake for 30 seconds (use a protective screen!). In the cylinder with zinc chloride, zinc dithizonate of red colour is formed; in the cylinder with mercury nitrate, mercury dithizonate of orange colour is formed. Add 50 ml of EDTA solution to each cylinder and

shake for 30 seconds. In the cylinder with zinc dithizonate, the colour changes to green due to the destruction of the complex and the separation of free dithizone. The colour does not change in the cylinder with mercury dithizonate.

CHELATOMETRIC TITRATIONS

Complexones are used most commonly as titrating agents. There are several methods of titration: direct, back, displacement and indirect. The end point of titration is established by indicators: acid-base, oxidation-reduction and metallochromic indicators. The latter are most commonly used; reagents belonging to the class of hydroxyazo compounds, including heterocyclic compounds, relate to them. According to the selectivity of interaction with metal ions, there are universal (non-specific) indicators, i.e., pyrocatechol violet, xylenol orange, murexide and Eriochrome Black T, and specific indicators, i.e., tiron, sulphosalicylic acid for the determination of iron (III), thiocyanate for the determination of iron (III) and cobalt, and thiourea for the determination of bismuth.

Experiment 144. Titration of the Copper Ion in the Presence of 1-(2-Pyridyl-Azo)-Naphthol-2(PAN) as Indicator

An important circumstance in selecting an indicator is the difference in the colour of the indicator and its combination with an ion being determined. In complex formation, the shift of the light absorption maximum of the most contrasting indicators reaches 70-120 nm.

The light absorption maximum of the 1-(2-pyridyl-azo)-naphthol-2 (PAN) indicator is at 470 nm at pH = 2-12 and, when combined with copper (II), it is at 560 nm within the same pH range, and that of the copper complexonate is at 820-840 nm. In the chelatometric titration of the copper ion, the violet colour of the complex of copper with PAN at the end point changes to green due to the superimposition of the yellow colour of PAN on the blue colour of the copper complexonate. For comparison,

the audience may be shown a non-contrasting change of colour in titrating calcium, magnesium and zinc by EDTA in the presence of Eriochrome Black T ($\Delta\lambda$ = 30-40 nm).

Reagents

Cupric sulphate, 0.1 *M* solution.
PAN, 0.01 per cent ethanol solution.
EDTA, 0.1 *M* solution.
Calcium chloride, 0.1 *M* solution.
Eriochrome Black T, 0.5 per cent mixture with sodium chloride.
Ammonia buffer solution (pH = 10). 54 g of ammonium chloride are mixed with 350 ml of 25 per cent ammonia solution and the mixture is diluted to 1 litre with water.

Procedure. In a cylinder, put 50 ml of copper sulphate solution and 100 ml of water; in another, put 50 ml of calcium chloride solution and 100 ml of water. To the first cylinder, add 20 ml of PAN solution; a violet colour appears. Add 60-70 ml of EDTA solution; the colour sharply changes to green. To the second cylinder, add about 50 mg of Eriochrome Black T and stir; a wine red colour appears. Add 60-70 ml of EDTA solution. The colour changes to blue. Point out the difference in contrast of the colour change in both cases.

Experiment 145. Titration of the Copper Ion in the Presence of Luminol as Luminescent Indicator

The chemiluminescence of luminol ceases when it is oxidized with hydrogen peroxide in the presence of copper ions if these ions are bound to EDTA. That is the basis of detection of the end point of titration in the chelatometric determination of copper ions [29].

Reagents

Cupric sulphate, 0.01 *M* solution.
EDTA, 0.01 *M* solution containing 20 ml of 3 per cent hydrogen peroxide solution in 1 litre.

Ammonia, 4 *M* solution.
Luminol, 0.01 per cent solution in 0.005 *M* alkaline solution.

Procedure. In a 1-litre flask, put 20 ml of copper sulphate solution and add 200 ml of ammonia solution and 30 ml of luminol solution. Heat to 80-90° C. Switch off the light. Titrate with EDTA solution. A blue luminescence appears from the very first drops. Titrate until the luminescence disappears.

Experiment 146. Titration of the Barium Ion in the Presence of Fluorexone as Metallofluorescent Indicator

In chelatometric titration, the equivalence point may be determined by the origination or extinction of fluorescence. If an indicator luminesces, it becomes extinguished in the presence of an element with which it forms a complex, and a luminescence originates at the equivalence point. If the complex of the element with the indicator luminesces, the luminescence is extinguished at the equivalence point when the element is titrated with EDTA.

Fluorexone (calcein, a fluorescein complexone) does not fluoresce in an alkaline medium. A bright green fluorescence is observed in the presence of the ions of barium, calcium and strontium. The fluorescence disappears when the metal ions are bound into strong complexonates [30].

Reagents
Barium chloride, 0.05 *M* solution.
EDTA, 0.05 *M* solution.
Calcein, 2 per cent solution.
Potassium hydroxide, 0.1 *M* solution.

Procedure. In a conical 300-ml flask, put 5 ml of barium chloride solution and 150 ml of potassium hydroxide solution. At the lecture, add 5 ml of indicator solution. Switch off the light and put the flask in the path of ultraviolet light (Fig. V-3). A green luminescence is observed. Titrate with EDTA solution until the luminescence disappears.

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CHAPTER X

Organic reagents

Organic reagents are now widely used in analytical chemistry. Their application is the basis of most modern methods of detecting, determining and separating elements [1-10].

In the general lecture course on analytical chemistry, only some fundamental problems of the theory and practical application of organic reagents may be expounded. By using organic reagents, many effective experiments may be performed with the formation of coloured compounds; it is possible to show the connection of the properties of elements with their position in the periodic system (see Chapter XIII), the difference in the reactions of the ions of elements with different degrees of oxidation (Experiments 99, 100), reactions of masking and demasking (Experiments 50, 143), of catalysis (Experiments 5, 29) and so forth.

Table X-1

SENSITIVITY OF SOME COLOUR REACTIONS

Ion	Reagent	Limit of detection, ppm
Mg^{2+}	Titanium yellow	0.01
Fe^{2+}	1,10-Phenanthroline	0.01
Cu^{2+}	Sodium diethyldithiocarbaminate	0.067
Zn^{2+}	Dithizone	0.01
Pb^{2+}	"	0.003
Cd^{2+}	"	0.01
Al^{3+}	Alizarin S	0.1
Zr^{4+}	"	0.02
BO_2^-	Curcumine	0.004
$Cr_2O_7^{2-}$	Diphenylcarbazide	0.02

To show the wide application of organic reagents in inorganic analysis, such methods may be indicated as chelatometric titration (see Chapter IX), the spectrometric and luminescent determination of metals (see Chapter II), and methods based on extraction (see Chapter VI), precipitation (see Chapters VI, IX), oxidation or reduction (see Chapter VIII), and so forth. Most indicators are organic compounds (see Chapters V, VIII). Due to the high sensitivity of the reactions of metal ions with organic reagents, the latter are widely used for detecting metals (Table X-1) [11].

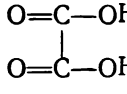
FUNCTIONAL ANALYTICAL GROUPINGS, DENTATION OF LIGANDS AND THE CHELATE EFFECT

The action of organic compounds as reagents is due to the presence of special atomic groupings in their molecules. At the lecture, the audience may be shown a table of the main types of atomic groupings and also reagents whose molecules contain these groups (Table X-2) [2].

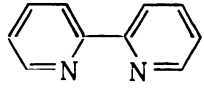
The most considerable effect occurs when such complexes are formed in which a ligand is bound to metal by two atoms or more, forming a metal chelate [12]. In this case, an important role is played by stabilization due to the ligand field, since ligand fields are stronger for multidentate chelates than for monodentate ones. The growth in the stability of complexes with an increase in ligand dentation is known as the chelate effect [12]. Examples of ligands of different dentation are given below:

Monodentate CN^-, PR_3, $CH_2=CH_2$

Bidentate

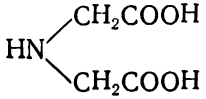


oxalic acid

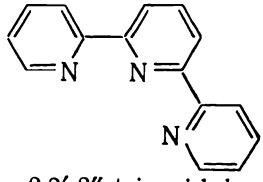


2,2′-dipyridyl

Tridentate

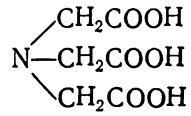


iminodiacetic acid



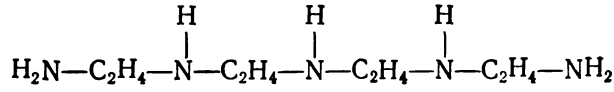
2,2′,2″-tripyridyl

Tetradentate



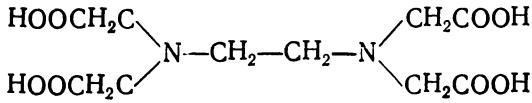
nitrilotriacetic acid

Pentadentate



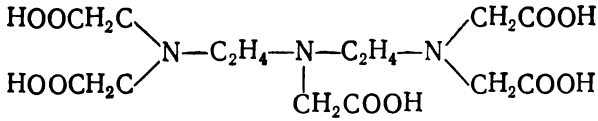
tetraethylenepentamine

Hexadentate



ethylenediaminetetraacetic acid

Octadentate



diethylenetriaminepentaacetic acid

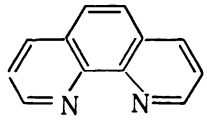
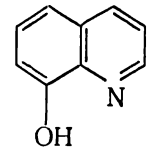
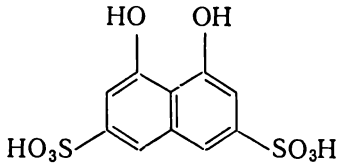
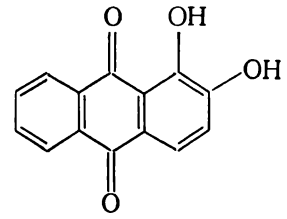
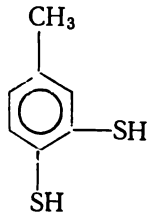
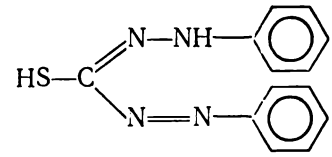
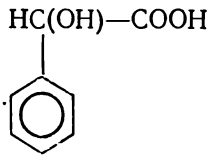
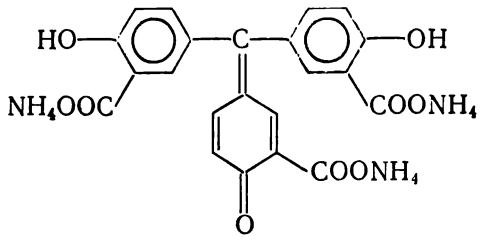
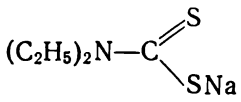
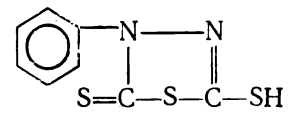
The stability of the metal chelate is a function of not only the number of members in a ring, but also the number of rings per the central metal ion in the complex. Hence, the larger the number of chelate rings that are formed, the more stable is the complex, provided other conditions are equal [for example, for Cu(II) complexes]:

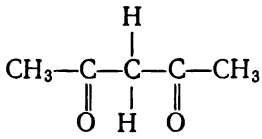
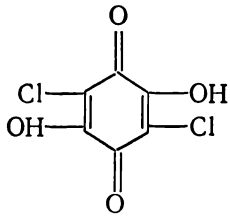
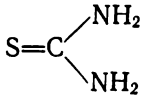
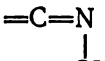
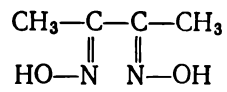
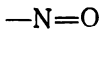
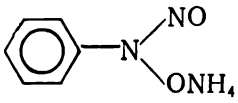
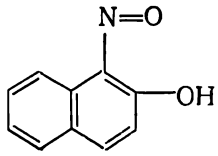
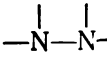
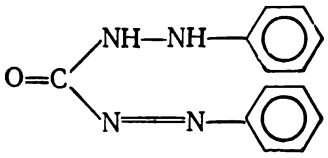
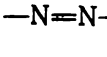
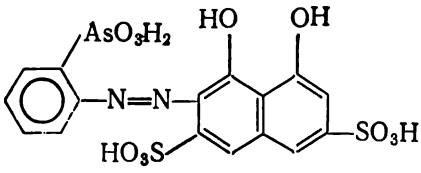
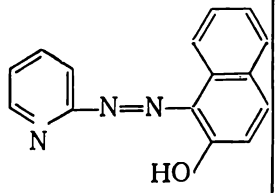
Ligand	log K_1
NH_3 (monodentate)	4.25
Ethylenediamine (bidentate) .	10.67
Triethylenetetramin (tetradentate)	20.5
EDTA (hexadentate)	18.8

Coordination compounds with five- and six-membered rings are the most stable (Chugaev's rule) [3]. There are complexes with 4-9 members in a ring (Table X-3). If an increase in ligand dentation is simultaneously accompanied with a growth in the conjugation chain, i.e., an increase in the mobility of π-electrons and a decrease in the excitation energy of the electrons of molecule, there is a growth in the stability of complexes by several orders and

Table X-2

MAIN COMPLEXING GROUPINGS IN ANALYTICAL REAGENTS

Grouping	Examples
—N=	 1,10-phenanthroline  8-hydroxyquinoline
—O—	 chromotropic acid  alisarin
—S—	 dithiol  dithizone
—C(=O)—O—	 mandelic acid  aluminon
—C(=S)—S—	 sodium diethyldithiocarbaminate  bismuthol II

Grouping	Examples
	 acetylacetone  chloranilic acid
	 thiourea
	 dimethylglyoxime
	 cupferron  1-nitrozo-2-naphthol
	 diphenylcarbazone
	 arsenazo I  1-(2-pyridylazo)-2-naphthol (PAN)

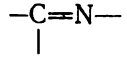
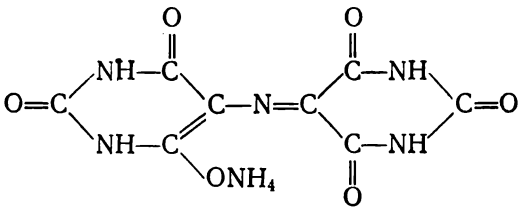
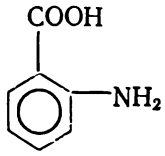
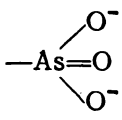
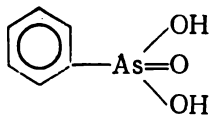
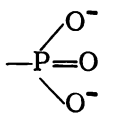
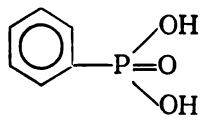
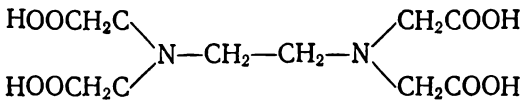
Grouping	Examples
	 murexide
—NH_2	 anthranilic acid
	$NH_2—CH_2—CH_2—\underset{\displaystyle H}{N}—CH_2—CH_2—\underset{\displaystyle H}{N}—CH_2—CH_2—NH_2$ triethylenetetramine
	 phenylarsonic acid
	 phenylphosphonic acid
	 ethylenediaminetetraacetic acid

Table X-3

CHELATE RINGS

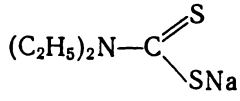
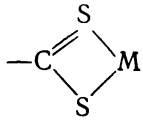
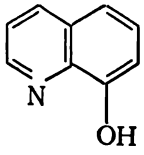
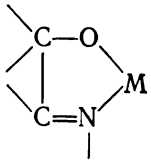
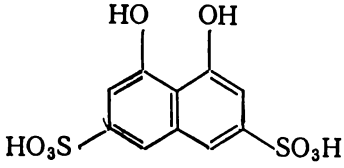
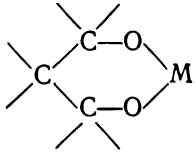
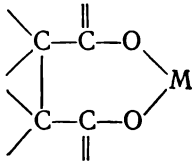
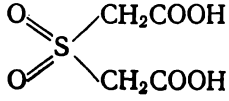
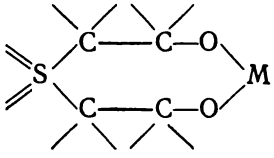
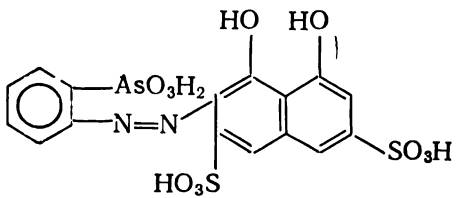
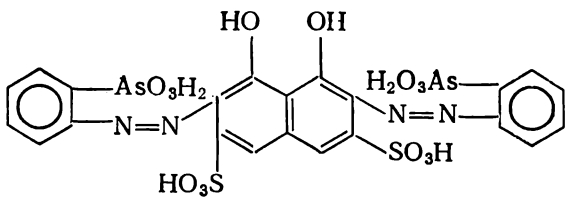
Ligand	Chelate ring
Sodium diethyldithiocarbaminate 	 four-membered
8-hydroxyquinoline 	 five-membered
Chromotropic acid 	 six-membered
Succinic acid HOOC—CH_2—CH_2—COOH	 seven-membered
Sulphonyl diacetic acid 	 eight-membered

Table X-4

COMPLEXES OF THORIUM (IV) WITH THE REAGENTS OF THE ARSENAZO GROUP

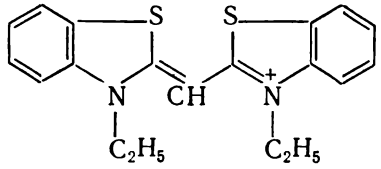
Reagent	Colour		Reaction conditions	Minimum concentration µg/ml
	of reagent	of complex		
Arsenazo I 	Pink	Violet	pH = 0.5 ÷ 1.5	0.2
Arsenazo III 	Red	Green	8*M* HCl	0.01

an increase in contrast of colour reactions and their sensitivity. Reagents of the arsenazo group may be demonstrated as an example [13]. It is expedient to show a table with the formulas of reagents and with the elements which produce characteristic reactions (Table X-4).

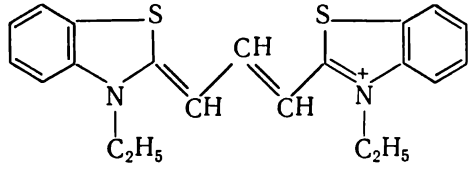
The difference in contrast of the transition of colour reactions of the mono- and bis-azo substituted molecules of chromotropic acid is due to the presence of two close vacant energy levels in the bis-azo substituted molecules of the reagents. The interaction of a bis-azo substituted reagent with metal ions leads to a sharp approximation of the higher filled and the lower vacant levels of energy and, consequently, to a strong bathochromic effect. The sharp contrast of colour change is not connected with the symmetry of a ligand molecule [14].

It is important to note that any change in the system of conjugate bonds leads mainly to the deepening of colour:

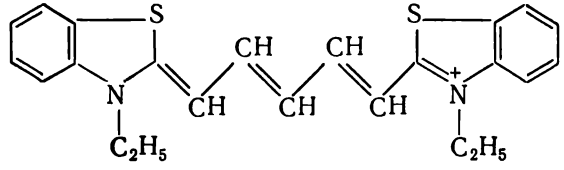
elongation of the conjugation chain



yellow

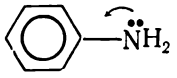


red

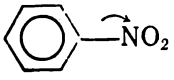


dark blue

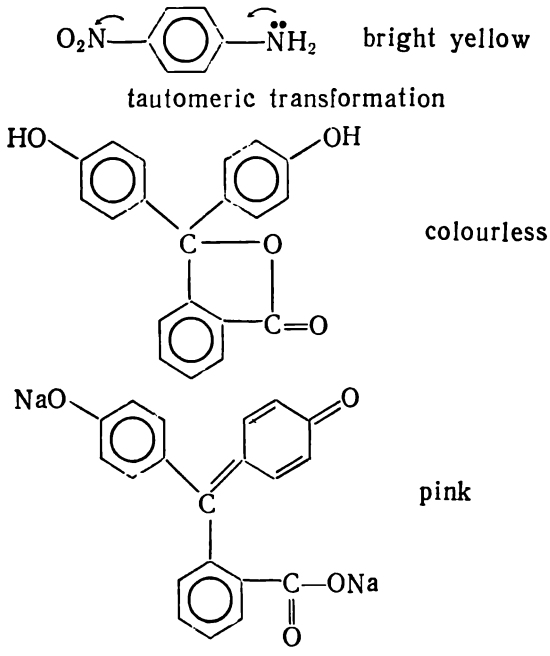
introduction of a substituent



colourless

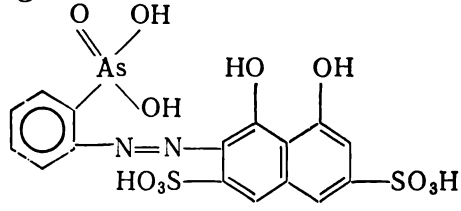


pale yellow

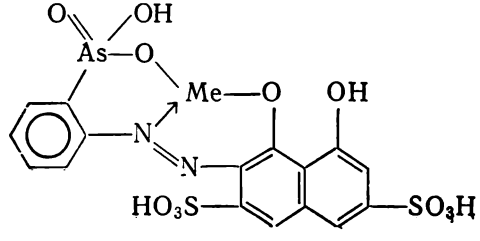


Experiment 147. Reaction of a Thorium Ion with Arsenazo I and Arsenazo III

Arsenazo I contains the functional *o*-arsono-*o*-hydroxyazo grouping



With metal ions, the reagent forms chelates with two six-membered rings; the presence of two rings in the complex makes it sufficiently stable



Aqueous solutions of the reagent have a pink colour; in a weakly acid medium, arsenazo I forms violet complexes. Arsenazo III forms, together with metal ions, more stable complexes having the composition M : R = 1 : 1 and 1 : 2, whereby some ions may be determined in strongly acid media. This increases the reaction selectivity and makes it possible to avoid the effect of side factors (hydrolysis, polymerization, anion effect, and so forth). The reactions of arsenazo III with elements are very contrasting; a colour change is observed from red to dark blue or emerald green (Zr, Th).

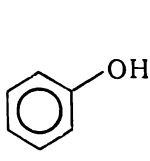
Reagents

Arsenazo I, 0.05 per cent solution.
Arsenazo III, 0.05 per cent solution.
Thorium sulphate, 1 per cent solution in 0.1 *N* hydrochloric acid solution.
Hydrochloric acid, concentrated.

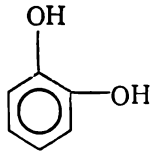
Procedure. In a cylinder, put 20 ml of thorium sulphate solution and 300 ml of water. At the lecture, divide the solution into two parts. To one cylinder, add 20 ml of arsenazo I solution; observe the colour change of the reagent from pink to violet. To the second cylinder, add 20 ml of arsenazo III solution and 100 ml of hydrochloric acid; observe the colour change from pink to emerald green.

Experiment 148. Reaction Between the Titanium Ion and Hydroxy Derivatives of Benzene

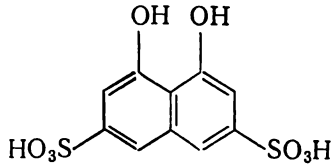
As a monodentate ligand, phenol forms a compound of low stability with the titanium (IV) ion. Titanium (IV) forms chelates of intense orange colour with pyrocatechol having OH groups in the ortho-position, and with chromotropic acid having OH groups in the peri-position; resorcinol, which contains OH groups in the meta-position, does not form complexes with the titanium (IV) ion:



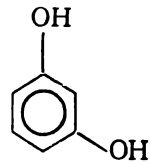
phenol



pyrocatechol



chromotropic acid



resorcinol

Reagents

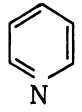
Phenol, pyrocatechol, resorcinol, chromotropic acid, 1 per cent solutions.

Titanium tetrachloride, 1 per cent solution in 1 *M* hydrochloric acid solution.

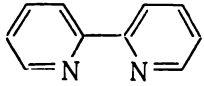
Procedure. Place four cylinders containing the solutions of phenol, pyrocatechol, resorcinol and chromotropic acid (400 ml each) with appropriate large labels that have structural formulas of reagents and that are turned to the audience. At the lecture, add 20 ml of titanium chloride solution to each solution and stir. The solutions in the cylinders with pyrocatechol and chromotropic acid become orange. In the other cylinders, the solutions are colourless.

Experiment 149. Reaction Between the Ferrous Ion and Heterocyclic Bases

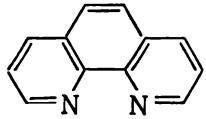
The heterocyclic bases 2,2′-dipyridyl and 1,10-phenanthroline form with iron (II) stable red chelates with five-membered rings; the complex with pyridine is unstable:



pyridine (Py)



2,2′-dipyridyl (Dipy)



1,10-phenenthroline (Phen)

$[Fe(Py)]^{2+}$	$\log \beta = 0.7$
$[Fe(Phen)]^{2+}$	$\log \beta_1 = 6.5$
$[Fe(Phen)_2]^{2+}$	$\log \beta_2 = 11.4$
$[Fe(Phen)_3]^{2+}$	$\log \beta_3 = 23.5$
$[Fe(Dipy)]^{2+}$	$\log \beta_1 = 4.2$
$[Fe(Dipy)_2]^{2+}$	$\log \beta_2 = 9.2$
$[Fe(Dipy)_3]^{2+}$	$\log \beta_3 = 17.1$

Reagents

Mohr's salt, 0.1 per cent solution in 0.1 *N* sulphuric acid solution.

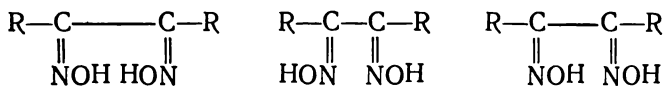
Pyridine.

2,2′-Dipyridyl, 1,10-phenanthroline, 0.25 per cent solutions of hydrochloride or hydrate in 0.1 *N* hydrochloric acid solution.
Sodium citrate, 10 per cent solution.

Procedure. Take three cylinders and in each of them put 20 ml of Mohr's salt solution, 20 ml of sodium citrate solution and 200 ml of water. At the lecture, add 10 ml of pyridine to one cylinder, 30 ml of 2,2′-dipyridyl solution to another cylinder, and 30 ml of 1,10-phenanthroline solution to the third cylinder. Observe the formation of red complexes in the last two cylinders.

STERIC EFFECTS

The formation and properties of complexes largely depend on the combination of the ligand structure and the stereochemistry of the complex. Hence, bulky ligands form less stable complexes with metal ions than analogous ligands of a smaller size. For example, $H_2NCH_2CH_2NH_2$ forms complexes of greater stability than $(CH_3)_2NCH_2CH_2N(CH_3)_2$. A molecule of tetramine $H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$ having an unbranched chain forms complexes of greater stability with Cu(II) than the amine $N(CH_2CH_2NH_2)_3$ having a branched chain, since a molecule of the first compound may coordinate to nitrogen atoms by the angles of a square, while a molecule of monoamine cannot fit into a plane square. Another example of the effect of steric factors on complexing is the interaction of three isomer forms of dioximes, syn-, anti- and amphi-, with metals. Compounds of an anti-form are the most stable; an amphi-form forms low-stable complexes, and a syn-form is not reactive at all:



Steric hindrances originate when a substituent either is added to a donor atom or is sufficiently close to it, caus-

ing the mutual repulsion of ligands and weakening the metal-ligand bond. This may be illustrated by data on the stability of the substituted copper (II) 8-hydroxyquinolinates (Fig. X-1) [12]. If the substituent is in a molecule of hydroxyquinoline in any position except position 2, good

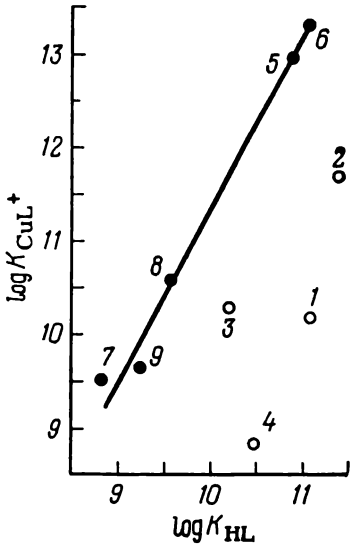
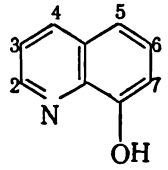


Fig. X-1. Dependence of the logarithms of stability constants of the complexes of copper (II) with the derivatives of 8-hydroxyquinoline on the logarithms of ionization constants of the corresponding reagents (20 °C, $\mu = 0.3$ in $NaClO_4$ solution): 1—2-methyloxine; 2 — 1, 2, 3-4-tetrahydro-10-hydroxyacridine; 3—8-hydroxy-2, 4-dimethylquinazoline; 4 — 8-hydroxy-4-methyl-2-phenylquinazoline; 5 — 8-hydroxyquinoline; 6 — 5-methyloxine; 7 — 8-hydroxycinnoline; 8 — 8-hydroxyquinazoline; 9 — 5-hydroxyquinoxaline. Light circles are reagents in which the substituent is next to the donor atoms of nitrogen.

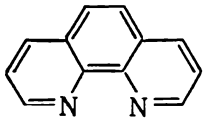
correlation between the stability of the complex and the basicity of the donor atom is observed:



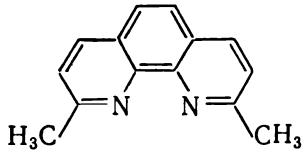
2-substituted compounds form complexes of lesser stability.

The following example may also be presented: the introduction of methyl groups into a phenanthroline molecule in the 2,9 position creates steric hindrances; this prevents from the formation of a complex with Fe(II), but

does not prevent from the formation of a Cu(I) complex:

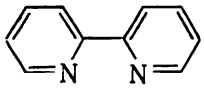


1,10-phenanthroline

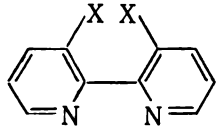


2,9-dimethyl-1,10-phenanthroline

Steric hindrances which originate in complexing with 3,3′-substituted 2,2′-dipyridyl are of different nature:



2,2′-dipyridyl

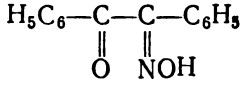


3,3′-substituted 2,2′-dipyridyl

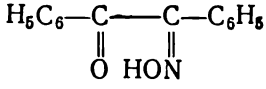
The introduction of alkyl groups in 3,3′-position causes a change in the plane configuration of a ligand and, consequently, reduces conjugation in the ligand and creates the metal-ligand bond stress.

Experiment 150. Effect of the Steric Structure of Benzoyl-monoxime on the Formation of the Complex with the Ferrous Ion

The reactivity of α- and β-benzoylmonoxymes is determined by the steric configuration:



α-form(anti)



β-form(syn)

The α-form gives bright dark blue compound with the ferrous ion, while the β-form does not react with it.

Reagents

Mohr's salt, 1 per cent solution in 0.1 *N* sulphuric acid solution.

α-Benzoylmonoxime, 1 per cent ethanol solution.
β-Benzoylmonoxime, 1 per cent ethanol solution.
Ammonia, 1 *M* solution.

Procedure. In a cylinder, put 20 ml of Mohr's salt solution and 300 ml of water. At the lecture, divide the solution into two parts. To one part, add 20 ml of α-benzoylmonoxime solution and 10 ml of ammonia solution. A dark blue colour appears. To the other part, add 20 ml of β-benzoylmonoxime solution and 5 ml of ammonia solution. The colour of the solution does not change.

Experiment 151. Formation of Complexes of Iron (II) and Copper (I) with Phenanthroline Derivatives

The 1,10-phenanthroline complex of iron (II) $[Fe(Phen)_3]^{2+}$ is a low-spin complex with a large stability constant and an intense red colour. The corresponding complex of copper (I) $[Cu(Phen)_2]^{+}$ is less stable. The introduction of methyl groups in the 2,9-position creates steric hindrances which prevent from the formation of the iron (II) complex; the high-spin complex of iron (II) formed is colourless. However, methyl groups do not prevent from the formation of copper (I) complexes, since the ligands are further away from one another owing to the larger radius of the cuprous ion, and steric hindrances are less.

Reagents

Cupric sulphate, 1 per cent solution.
Mohr's salt, 1 per cent solution in 0.1 *N* sulphuric acid solution.
1,10-Phenanthroline, 0.25 per cent solution of hydrochloride or hydrate in 0.1 *N* hydrochloric acid solution.
2,9-Dimethyl-1,10-phenanthroline (neocuproin), 0.03 per cent ethanol solution.
Hydroxylamine hydrochloride.
Sodium citrate, 10 per cent solution.
Acetate buffer solution (pH = 4.5). 80 g of sodium acetate are dissolved in water, 60 ml of 80 per cent acetic acid solution are added and the solution is diluted to 500 ml with water.

Procedure. In a cylinder, put 10 ml of Mohr's salt solution, 30 ml of sodium citrate solution and 300 ml of water. At the lecture, divide the solution into two parts. To one part, add 20 ml of 1,10-phenanthroline solution and observe the formation of a red phenanthroline complex of iron. To the other part, add 20 ml of neocuproin solution; the colour of the solution does not change.

To another cylinder, put 20 ml of copper sulphate solution and add 1 g of hydroxylamine hydrochloride, 60 ml of acetate buffer solution and 300 ml of water. At the lecture, divide the solution into two parts. To one part, add 20 ml of 1,10-phenanthroline solution. To the other part, add 20 ml of neocuproin solution. An intense orange colour of a copper complex appears in both cylinders.

Experiment 152. Formation of Complexes of Aluminium with 8-Hydroxyquinoline Derivatives

A chelate compound of the aluminium ion with 8-hydroxyquinoline, $Al(C_9H_6NO)_3$, is slightly soluble in water, but soluble in chloroform. The solution of aluminium 8-hydroxyquinolinate in chloroform has a yellow colour; this is used for the photometric determination of aluminium. Metal ions with small radii cannot form complexes with three anions of 2-methyl-8-hydroxyquinoline. The small dimensions of the aluminium ion make it possible to bind only two anions of 2-methyl-8-hydroxyquinoline. The complex of aluminium with two ligands has a positive charge; it is soluble in water and is not extracted by chloroform. This quality is used for separating aluminium ions from zinc and other larger cations.

Reagents

Aluminium chloride, 1 per cent solution.
8-Hydroxyquinoline, 5 per cent ethanol solution.
2-Methyl-8-hydroxyquinoline, 5 per cent ethanol solution.
Ammonia, 2 *M* solution.

Procedure. In a cylinder, put 30 ml of aluminium chloride solution and 300 ml of water. At the lecture, divide the solution into two parts. To one part, add 30 ml of

8-hydroxyquinoline solution and, to the other, 30 ml of 2-methyl-8-hydroxyquinoline solution. Add 10 ml of ammonia solution to each of the two cylinders and observe the formation of a precipitate in the first cylinder.

EFFECT OF LIGAND BASICITY ON THE STABILITY OF COMPLEXES

The stability of complexes of metal ions with a small ionic radius, a higher oxidation state and low polarizability correlates well with ligand basicity [15]:

$$\log \beta \approx A\mathrm{p}K_a + B$$

where A and B = constants depending on the nature of the metal ion and the ligand. The value B may also characterize the metal-ligand π-bond.

Probably the same factors affect the protonation of ligands and the formation of σ-bonds between ligands and the metal ion.

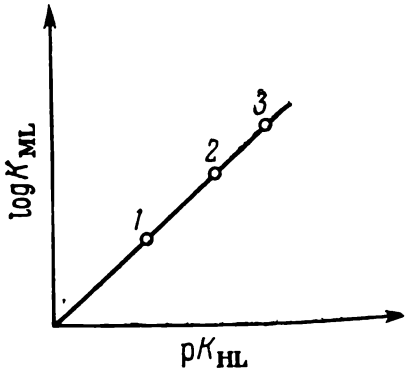


Fig. X-2. Dependence of the stability of complexes on the basicity of the nitrogen atom of the following acids:
1 — phenyliminodiacetic; 2 — methyliminodiacetic; 3 — isohexyliminodiacetic

The linear dependence between the basicity of the donor atom and the stability of complexes may be shown by taking the example of complexones (Fig. X-2).

A change in the basicity of the donor atoms of the ligand is connected with the introduction of electrophilic or nucleophilic substituents. When the substituents are introduced, the direct dependence between the basicity of the donor atom of the ligand and the coordination ability of

the ligand is preserved if the substituents that are introduced do not participate in complex formation and if their bulk does not cause steric hindrances. This principle may be illustrated by the data in Fig. X-1.

Experiment 153. Reaction of the Copper Ion with 8-Hydroxyquinoline and 5,7-Dibromo-8-hydroxyquinoline

The introduction of substituents (Cl, Br, I) into a 8-hydroxyquinoline molecule increases the basicity of the atom of nitrogen or oxygen; this makes it possible to obtain complexes of substituted 8-hydroxyquinoline with iron (III), copper (II), titanium (IV) and vanadium (V) that are more stable in an acid medium than complexes with 8-hydroxyquinoline.

Reagents

Cupric sulphate, 1 per cent solution.
8-Hydroxyquinoline, 1 per cent ethanol solution.
5,7-Dibromo-8-hydroxyquinoline, 1 per cent ethanol solution.
Hydrochloric acid, 2 *M* solution.

Procedure. In a cylinder, put 40 ml of copper sulphate solution and dilute to 400 ml with water. At the lecture, add 40 ml of hydrochloric acid solution. Divide the solution into two parts. To one part, add 20 ml of 8-hydroxyquinoline solution. A precipitate is not formed. To the other part, add 20 ml of 5,7-dibromo-8-hydroxyquinoline solution. A yellow flaky precipitate is formed.

EFFECT OF THE SOLVENT NATURE ON THE COLOUR OF METAL CHELATES

Solutions of chelate compounds with organic ligands may have different colour, depending on the solvent nature. This may be observed by taking the example of the azo derivatives of 8-hydroxyquinoline of the following

structure (Table X-5) [16]:

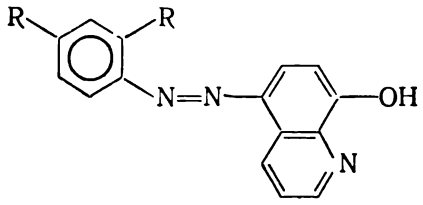


Table X-5

EFFECT OF THE SOLVENT NATURE ON THE COLOUR OF COMPLEXES WITH 2,4-DINITROBENZENE-(1-AZO-5)-8-HYDROXYQUINOLINE

Element	Colour of complexes in			
	benzene	chloroform	*n*-butanol	cyclohexanone
Cd^{2+}	Brown-yellow	Yellow-brown	Pink	Red-violet
Zn^{2+}	Red-pink	Red-pink	Pink	Pink
Ni^{2+}	Crimson	Violet	Red-violet	Dark blue-violet

Experiment 154. Colour of Nickel 2,4-Dinitrobenzene-(1-Azo-5)-8-Hydroxyquinolinate in Various Solvents

In an aqueous solution, nickel (II) forms a brown-violet suspension of a chelate compound with azo derivatives of 8-hydroxyquinoline. A colour change is observed when the complex is extracted by various solvents.

Reagents

Nickelous chloride, 1 per cent solution.
2,4-Dinitrobenzene-(1-azo-5)-8-hydroxyquinoline, 0.05 per cent acetone solution.
Benzene.
n-Butanol.
Cyclohexanone.

Procedure. Take three cylinders and in each of them put 10 ml of nickel chloride solution and 200 ml of water. At the lecture, add 20 ml of acetone solution of the reagent to each cylinder. A brown-violet suspension of the nickel

chelate is formed everywhere. To one cylinder, add 100 ml of benzene, to another, 100 ml of *n*-butanol, and to the third, 100 ml of cyclohexanone. Shake each cylinder (use a protective screen!). The difference in the colour of the organic layers is seen after the separation of phases: crimson in benzene, red-violet in *n*-butanol, and dark blue-violet in cyclohexanone.

SELECTIVITY OF ORGANIC REAGENTS

The selective action of organic reagents is due to the presence of functional analytical groupings in their molecules.

A table may be shown to illustrate the dominant complex formation of metal ions in conformity with the electron structure and the nature of the donor atom of the ligand (Table X-6).

Table X-6

DIVISION OF METALS IN TERMS OF ELECTRONIC STRUCTURE

Ligand	Metals
O-Ligands	Metals giving ions resembling the inert gases Li Be B Na Mg Al K Ca Sc Zr Rb Sr Y Hf Cs Ba La, Ce-Lu Th
N-Ligands	Metals with ions having partly filled *d* or *f*-orbitals Ti V Cr Mn Fe Co Ni Cu^{II} RE elements Nb Mo Tc Ru Rh Pd Ag^{II} and actini- Ta W Re Os Ir Pt Au^{III} des
S-Ligands	Metals with ions having filled *d*-orbitals Cu(I) Zn Ga Ge As Ag(I) Cd In Sn Sb Tl Au(I) Hg Tl Pb Bi Po

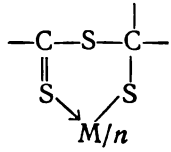
The selectivity of a reagent may be increased by introducing substituents, which create steric hindrances in co-

ordination (see Experiments 150-152). Sufficiently high selectivity may be attained in separate cases by pH selection, reagent concentration and also the use of masking agents, which increase the difference in the behaviour of metal ions (see Experiments 13, 143) [9, 10, 17-22].

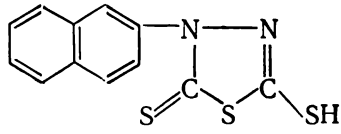
Characteristic Functional Analytical Groupings

Experiment 155. Reaction of the Tellurium Ion with Bismuthol Derivatives

Reagents whose molecules contain two thiocarbonyl groups form coloured chelate compounds with the tellurium (IV) ion



Such organic reagents are 5-mercapto-1,3,4-thiadiazolthione-2 (bismuthol I) and its derivatives, such as:



5-mercapto-3-(naphthyl-2′)-1,3,4-thiadiazolthione-2

When a solution of this reagent is added to a strongly acid solution (up to 9 *M* H_2SO_4), which contains tellurium (IV), an orange precipitate is formed that is insoluble in water but soluble in organic solvents: benzene, chloroform, cyclohexane, and so forth [23].

Reagents

Tellurium dioxide. 0.1 g of tellurium dioxide is dissolved in 100 ml of 2 *M* hydrochloric acid solution.

Potassium 5-mercapto-3-(naphthyl-2′)-1,3,4-thiadiazolthione-2, 0.1 per cent solution.

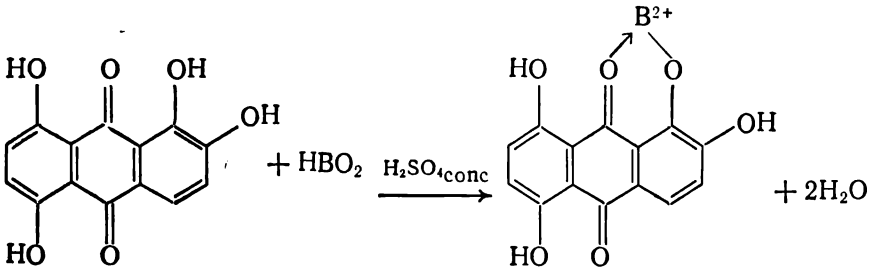
Hydrochloric acid, 2 *M* solution.

Benzene.

Procedure. In a cylinder, put 10 ml of tellurium dioxide solution and 200 ml of hydrochloric acid solution. At the lecture, add 10 ml of reagent solution; an orange precipitate is formed. Extract the precipitate with 100 ml of benzene; an orange solution is obtained.

Experiment 156. Complex Formation Between the Borate Ion and Quinalizarin

Reagents which belong to the polyoxyanthraquinone group, such as quinalizarin and carmine, form coloured compounds with boron ions in a concentrated sulphuric acid medium. In this medium, boron has the form BO^+ or $B(OH)^{2+}$ and possibly B^{3+} [24, 25], and forms chelate compounds with the reagents:



violet cornflower blue

The reacton of the boron ion with quinalizarin is sensitive, its limit of detection being 0.1 ppm.

Among the photometric methods of boron determination, the most sensitive is the one with the utilization of curcumine; the molar absorptivity of the complex $\bar{\varepsilon}$ is $1.8 \cdot 10^5$.

Reagents

Quinalizarin, 0.01 per cent solution in concentrated sulphuric acid.

Boric acid.

Procedure. In a cylinder, put 400 ml of quinalizarin solution. (The solution is violet.) At the lecture, divide the solution into two parts. Keep one part for reference. To

the other part, add 10-20 mg of boric acid (or its salt) and stir. The solution becomes bright cornflower blue.

Note. Care should be taken in carrying out the experiment with concentrated sulphuric acid. A solution of boric acid or of its salts must not be added to a quinalizarin solution containing concentrated sulphuric acid.

Experiment 157. Reaction of the Antimonous Ion with 1-(2-Pyridylazo)-naphthol

PAN forms with ions of multivalent metals coloured complexes which may be extracted by organic solvents: chloroform and benzene. The selectivity of metal determination with the utilization of PAN may be increased by selecting suitable pH values, masking agents and organic solvents. For example, antimony (III) reacts with PAN in 2 *M* hydrochloric acid solution; determination is interfered only with copper, which may be masked by thiourea. Cyanides make it possible to mask nickel, zinc, cadmium, cobalt and copper. The colour of complexes of metal ions with PAN ranges from orange to red. In acid solutions at pH = 2, PAN exists in a protonated form, H_2R^+, of yellow-green colour; at pH = 3 ÷ 11, it exists in the form of a neutral molecule, HR, which in organic solvents produces a yellow solution. In alkaline solutions at pH = 11, PAN forms R^- ions of red colour.

Reagents

Antimonous chloride, 1 per cent solution in 2 *M* hydrochloric acid solution.
PAN, 0.05 per cent acetone solution.
Thiourea, 10 per cent solution.
Potassium bromide, saturated solution.
Hydrochloric acid, 6 *M* solution.
Benzene.
Cupric sulphate, 1 per cent solution.

Procedure. In a cylinder, put 10 ml of copper sulphate solution and 100 ml of water. At the lecture, add thiourea solution until the copper-thiourea precipitate formed is dissolved. Then, add 50 ml of potassium bromide solution,

50 ml of hydrochloric acid solution, 20 ml of PAN solution and 100 ml of benzene, and stir. After the separation of phases, it may be observed that the organic layer is coloured yellow by the reagent. Add 10 ml of antimony chloride solution and stir again. The organic layer becomes red as a result of the formation of the complex of antimony with PAN.

Specific Reactions Based on the Synthesis of Organic Reagents

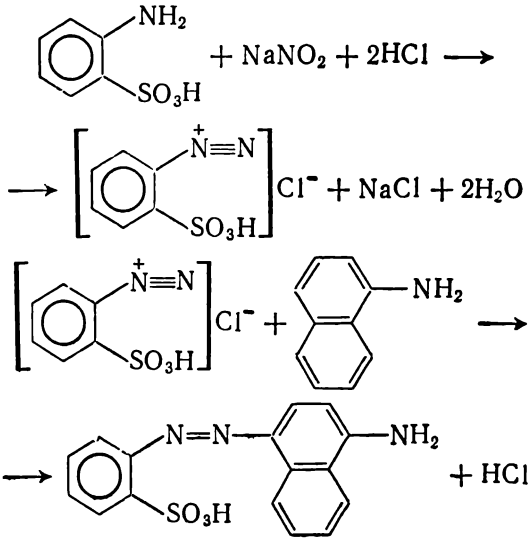
Reactions of ion detection are very effective when not the prepared reagent, but the components from which it may be formed during the reaction (homogeneous precipitation, see Chapter VI) are introduced. The reactions of organic reagent synthesis are the basis of the detection and determination of nitrate, nitrite and ammonium ions, and also bromine, chlorine and other oxidizing agents.

Ions being determined participate in the synthesis of an organic compound, and this determines the specificity of the reaction.

Experiment 158. Specific Reaction of the Nitrite Ion Based on the Synthesis of an Azo Compound (Griess' Reaction)

The Griess reaction proceeds in two stages: the diazotization of primary amine by nitrite ions, with the formation of diazonium salt; the combination of diazonium salt with phenols or aromatic amines, with the formation of coloured azo compounds [26]. The diazotization rate depends on the concentration of the nitrite ion, temperature and other factors, and also on amine properties. The colour of the azo compound that is formed also depends on the type of amine. The excess of the nitrate ion that remains after diazotization causes side processes: nitrozation, or oxidation of azo constituents, and this leads to a change in or even decomposition of the azo compound.

Sulphanilic acid may be used as a diazo constituent, and α-naphthylamine may be used as an azo constituent;



The reaction is very sensitive; the limit of detection is 0.2 ppm.

Reagents

Griess reagent. A mixture of 0.1 g of α-naphthylamine, 1 g of sulphanilic acid and 8.9 g of tartaric acid is ground in a mortar. One gram of the mixture is dissolved in 100 ml of water.

Potassium nitrite, 0.01 per cent solution, freshly-prepared.

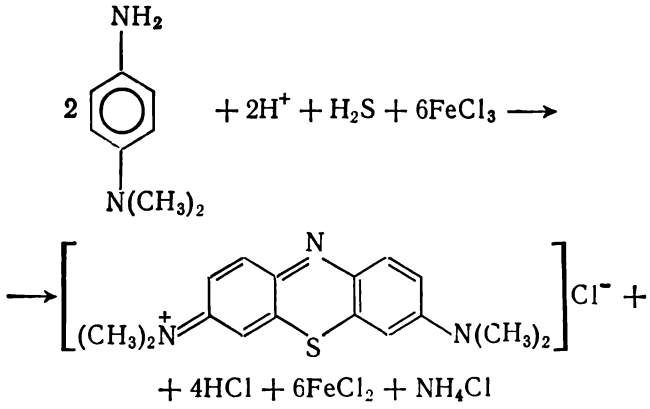
Procedure. *Variant I.* In a cylinder, put 100 ml of Griess reagent solution and 200 ml of water. At the lecture, add 5 drops of potassium nitrite solution from a pipette and stir. Somewhat later, a faint pink colour appears, and its intensity gradually grows. A brownish precipitate may even be formed if the nitrite concentration is large.

Variant II. In a cylinder, put 2 ml of potassium nitrite solution and 300 ml of water. At the lecture, add 50 ml of Griess reagent solution; a pink colour appears. Pour the solution into a sink, rinse the cylinder, pour 300 ml of water into it and add 100 ml of Griess reagent solution. The pink colour reappears. This proves that the sensitivity of the reaction is exceptionally high.

Note. In the first cylinder, the colour of the solution obtained rapidly disappears due to the destruction of the azo compound by an excess of nitrous acid.

Experiment 159. Detection of Hydrogen Sulphide by the Formation of Methylene Blue

Hydrogen sulphide forms the methylene blue dye [27] with N,N-dimethyl-p-phenylenediamine and in the presence of ferric chloride:



The reaction makes it possible to detect 0.0002 mg of hydrogen sulphide.

When hydrogen sulphide is in very small quantities, the colour develops in 30 minutes. When acidification is insufficient, the reagent itself produces a red colour with ferric chloride.

Reagents

Dimethyl-p-phenylenediamine hydrochloride. One gram of the reagent is dissolved in 300 ml of concentrated hydrochloric acid.

Ferric chloride, 10 per cent solution in 1 *M* hydrochloric acid solution.

Hydrogen sulphide, saturated solution.

Procedure. In a cylinder, put 300 ml of dimethyl-*p*-phenylenediamine solution. At the lecture, add 100 ml of ferric chloride solution and 1-2 ml of hydrogen sulphide solution. An intense colour of methylene blue appears.

Experiment 160. Detection of the Ammonium Ion by the Reaction of Dye Formation

To determine the ammonium ion, use is made of the reaction between the ammonium ion and hypobromite or hypochlorite and phenol, with the formation of a stable, soluble indophenol dye. The reaction probably proceeds via the formation of halogenamine (NH_2Br, NH_2Cl), which forms quinochloramine or quinobromamine with phenol. The latter, in turn, combines with another phenol molecule, forming indophenol [28]. The reaction products may be extracted by diethyl ether or xylene.

Reagents

Phenol. 70 g of phenol are dissolved in 15 ml of ethanol; 20 ml of acetone are then added and the solution is diluted with ethanol to 100 ml.

Sodium phenolate. Immediately before utilization, 10 ml of phenol acetone solution are mixed together with 10 ml of 30 per cent sodium hydroxide solution, and the solution obtained is diluted to 50 ml with water.

Sodium hypochlorite, 2 per cent solution.

Ammonium chloride, 0.03 per cent solution.

Procedure. In a cylinder, put 10 ml of ammonium chloride solution and 200 ml of water. At the lecture, add 30 ml of sodium phenolate solution and 15 ml of sodium hypochlorite solution. Observe the formation of the dark blue dye.

Effect of pH on the Selectivity of Reagents

Many organic reagents are weak acids; therefore, the production of different forms of a reagent depends on the pH of the solution. A diagram of the state of EDTA may be a good illustration (see Fig. IX-5).

Hence, the concentration of the reaction form of a reagent and, consequently, the yield of a complex, change as the hydrogen ion concentration changes. It is expedient to show the audience tables of the selective action of some organic reagents, for example, the pH of precipitation of metal 8-hydroxyquinolinates (Table X-7) [29], and also

Table X-7

pH OF PRECIPITATION OF METAL HYDROXYQUINOLINATES

Ion	pH of precipitation	Ion	pH of precipitation
Al^{3+}	$\geqslant 4.7$	Mg^{2+}	$\geqslant 8.7$
W^{VI}	3.3-3.5	Cu^{2+}	5.3-14.5
Fe^{3+}	2.8-11.2	Ni^{2+}	$\geqslant 4.6$
Ca^{2+}	$\geqslant 9.2$	Ti^{IV}	4.8-8.6
Co^{2+}	$\geqslant 4.9$	Zr^{IV}	4.7-12.5

Mendeleyev's table with crosshatched blocks: precipitation by cupferron in 1 *M* sulphuric acid.

I	II	III	IV	V	VI	VII	VIII		I	II	III	IV	V	VI	VII	0
H																He
Li	Be										B	C	N	O	F	Ne
Na	Mg										Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac**	Ku														

Completely

Partially

* *Lanthanoids*

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

** *Actinoids*

Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	(No)	Lr

An increase in the concentration of ligand ions may lead to the formation of a complex with a large number of coordinated ligands, owing to which the colour may change (Table X-8) [30] (see also Experiment 40).

Hydrogen ion concentration affects the state of metal ions in solutions. Strongly hydrolized ions (zirconium, titanium, etc.) selectively react with organic reagents in a

Table X-8

EFFECT OF pH ON THE COMPOSITION AND COLOUR OF IRON COMPLEXES

Reagent	Complex	pH	Colour
Sulphosalicylic acid	$[Fe(Sal)]^+$	1-4	Violet-pink
	$[Fe(Sal)_2]^-$	4-8	Red-brown
	$[Fe(Sal)_3]^{3-}$	> 8	Yellow
Pyrocatechol	$[Fe(Pyr)]^+$	< 5	Green
	$[Fe(Pyr)_2]^-$	5-9	Violet
	$[Fe(Pyr)_3]^{3-}$	> 9	Red

strongly acid medium. A table showing metal ion precipitation by phenyl arsonic acid in 10 per cent sulphuric acid may be drawn up similarly to the table given above.

Experiment 161. Reaction of Palladium and Nickel Ions with Dimethylglyoxime at Different pH Values

Like the nickel ion; the palladous ion has a coordination number of 4 in respect to dimethylglyoxime (H_2D) and forms a plane square complex that is water-insoluble. However, unlike nickel dimethylglyoximate, palladium dimethylglyoximate is stable in acid solutions, while it dissolves in an alkaline medium, exhibiting the ability to additionally coordinate hydroxyl ions. In an alkaline medium in the presence of an oxidizing agent, nickel forms with dimethylglyoxime a red water-soluble complex [30]; this property is the basis of the photometric method of nickel determination. The complex has the formula $[Ni(D)_3]^{2-}$, where nickel is tetravalent. As an oxidizing agent, the widest use is made of bromine, persulphate or iodine.

Reagents

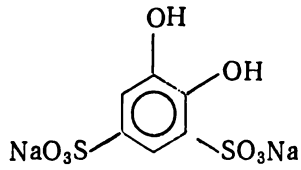
Nickelous sulphate, 10 per cent solution.
Dimethylglyoxime, 1 per cent ethanol solution.
Palladium tetrachloro complex $[H_2PdCl_4]$, 1 per cent solution in 2 *M* hydrochloric acid solution.

Ammonia, 25 per cent solution.
Ammonium persulphate, 10 per cent solution.
Hydrochloric acid, 2 *M* solution.

Procedure. In a cylinder, put 20 ml of nickel sulphate solution, 20 ml of palladous chloride solution and 200 ml of water. At the lecture, divide the solution into two parts. To one part, add an ammonia solution until dark blue nickel ammoniate is formed, and then 100 ml of dimethylglyoxime solution. A pink precipitate of nickel dimethylglyoximate is formed. Add 50 ml of ammonium persulphate solution; the precipitate dissolves, forming the red complex $[NiD_3]^{2-}$. To the other part, add 100 ml of hydrochloric acid solution and 100 ml of dimethylglyoxime solution. A yellow precipitate of palladium dimethylglyoximate is formed. A green solution of nickel sulphate may be seen above the precipitate.

Experiment 162. Reaction Between Tiron and the Ferric Ion

The disodium salt of 1,2-dioxybenzene-3,5-disulphonic acid (tiron)



having two OH groups in the ortho-position, is a reagent for the ferric ion. The characteristic spectra of complexes are due to the charge transfer with the displacement of an electron from a ligand to a metal ion. The acidity constants pK_a of phenol groups that determine its complexing power are 7.66 and 12.6; therefore, at $pH \leqslant 5$, the concentration of a ligand of diphenolate R^{2-} constitutes only $0.5 \cdot 10^{-10}$ part of the total concentration of tiron, and the formation of the complexes $[FeR]^+$ of violet colour with $\log \beta = 20.7$ is the most probable. At large pH-values, the complexes $[FeR_2]^-$ of red colour with $\log \beta_2 = 37.9$ and

$[FeR_3]^{3-}$ of yellow colour with $\log \beta_3 = 48.9$ (20° C, $\mu =$ $= 0.1$) are formed.

Reagents

Ferric chloride, 1 per cent solution in 0.1 *N* hydrochloric acid solution.
Tiron, 0.1 per cent solution.
Ammonia, 2 *M* solution.
Acetic acid, 2 *M* solution.

Procedure. In three cylinders, put 10 ml of total chloride solution, 2 ml of acetic acid solution and 200 ml of water, respectively. At the lecture, pour 30 ml of tiron solution in each cylinder. Observe the formation of the violet complex. Add 4 ml of ammonia to the second cylinder; a red colour appears. Add 20 ml of ammonia solution to the third cylinder; a yellow colour appears.

Application of the Reactions of Oxidation-Reduction of Organic Reagents to Ion Detection

Many organic substances are capable of being oxidized or reduced with the formation of coloured products; this makes it possible to use them for detecting some ions of oxidizing or reducing agents. For example, benzidine and diphenylamine are reagents for oxidizing ions, while cacotheline [31] makes it possible to detect reducing ions.

Experiment 163. Detection of the Stannous Ion by Cacotheline

Cacotheline is a nitro compound of brucine. The stannous ion reduces cacotheline in acid solutions to products of a violet colour. The reaction is sensitive: the limit of detection is 4 ppm. Tin detection is interfered with ferrous ions in the presence of phosphate ions.

Reagents

Cacotheline, saturated solution.
Tin tetrachloride, 1 per cent solution in 6 *M* hydrochloric acid solution.
Granular lead.

Procedure. In a conical flask, put 50 ml of tin tetrachloride solution and 100 ml of water. At the lecture, add granular lead and heat while stirring. Stannic ions are reduced to stannous ions. Pour the solution into a cylinder and add 30 ml of cacotheline solution. A colour change of the solution from yellow to violet is observed.

Extraction of Complexes with Organic Reagents

A large part of organic reagents are compounds that convert metal ions to products which are easily extractable with water-immiscible organic solvents [32-39]. If an organic ligand forming a chelate compound with a metal ion fills in all coordination sites or creates steric hindrances to the coordination of water molecules, the compound

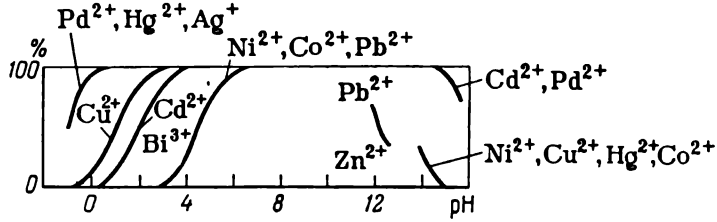


Fig. X-3. Diagram of metal dithizonate extraction

is extracted with a large set of solvents, regardless of their nature. Complexes in which organic ligands fill in not all coordination sites are extracted with solvents whose molecules are coordinated to metal ions [32]. Ion associates formed by large organic cations, for example, by basic dyes and complex metal anions, are extracted with different organic solvents [39, 40].

Extraction of coloured complexes with organic reagents is widely used for the extraction-photometric determination of element traces [1, 2, 11, 13, 25, 32, 37, 39].

Extraction is one of the best methods of separation. The extractability of elements depends on many factors; pH, temperature, reagent concentration, the type of solvent.

As an example of selective extraction, it is expedient to present a diagram of extraction of the dithizonates and

hydroxyquinolinates of metals at different pH values (Figs. X-3 and X-4) and also a table of the conditions for

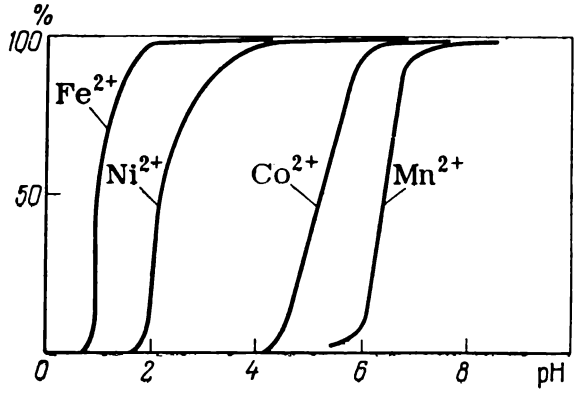


Fig. X-4. Diagram of metal 8-hydroxyquinolinate extraction

metal cupferronate extraction with chloroform (Table X-9) [35, 36].

Table X-9

CONDITIONS OF METAL CUPFERRONATE EXTRACTION WITH CHLOROFORM

Ion	Extraction conditions (pH)	Ion	Extraction conditions (pH)
Co^{2+}	> 4.5	Bi^{III}	2-12
Be^{2+}	> 3	Sb^{III}	0-9
Cu^{2+}	2-10	Ti^{IV}	0-4
Cd^{2+}	> 7	Zr^{IV}	0-3
Fe^{3+}	2-10		
Al^{3+}	3.5-9.5		

Experiment 164. Extraction of Nickel and Cobalt Dimethylglyoximates

In a plane molecule of nickel dimethylglyoximate, the presence of a hydrogen bond between OH groups impedes water coordination and explains the easiness of its extraction with chloroform. A similar octahedral complex of cobalt with water molecules in the inner sphere is not ex-

tracted with the solvents of the chloroform type, but is extracted with oxygen-bearing solvents (alcohols).

Reagents
Nickelous sulphate, 0.1 per cent solution.
Dimethylglyoxime, 1 per cent ethanol solution.
Cobaltous chloride, 1 per cent solution.
Ammonia, 25 per cent solution.
Chloroform.

Procedure. In a cylinder, put 10 ml of nickel sulphate solution and 100 ml of water; in another cylinder, put 50 ml of cobalt chloride solution and 100 ml of water. At the lecture, add 50 ml of dimethylglyoxime and 10 ml of ammonia solution to each cylinder. In the first cylinder, a pink precipitate of nickel dimethylglyoximate is formed, and in the second, a red-brown solution of cobalt dimethylglyoximate is formed. To each cylinder, add 100 ml of chloroform and stir. After lamination, the organic phase in the first cylinder is coloured yellow by nickel dimethylglyoximate, and in the second, the organic phase is colourless.

Note. Cobalt dimethylglyoximate may be extracted with isoamyl alcohol.

Experiment 165. Extraction of Cobalt 8-Hydroxyquinolinate

Unlike many metals, cobalt (II) forms with 8-hydroxyquinoline a plane square complex. However, two water molecules, which are characteristic of such types of complexes, are weakly bound, and this determines its extraction with chloroform.

Reagents
8-Hydroxyquinoline, 1 per cent chloroform solution.
Cobaltous chloride, 1 per cent solution.

Procedure. In a cylinder, put 10 ml of cobalt chloride solution and 100 ml of water. At the lecture, add 100 ml of chloroform 8-hydroxyquinoline solution. After stirring, orange cobalt 8-hydroxyquinolinate is formed in the chloroform layer.

Experiment 166. Extraction of the Ion Associate of the Thiocyanate Complex of Vanadium and the Pyridinium Ion

Vanadium (IV) forms with thiocyanate ions, the dark-blue complex of $[VO(SCN)_3]^-$ composition [38]. When vanadium (V) reacts with thiocyanate ions, a complex of the same composition is formed, since vanadium (V) is reduced by thiocyanate ions to vanadium (IV). In the presence of pyridine, the thiocyanate complex is extracted with chloroform in the form of an ion associate.

Reagents
Ammonium vanadate, 1 per cent solution.
Ammonium thiocyanate, 10 per cent solution.
Sulphuric acid, 7 *M* solution.
Pyridine.
Chloroform.

Procedure. In a cylinder, put 5 ml of ammonium vanadate solution, 10 ml of sulphuric acid solution and 100 ml of water. At the lecture, add 50 ml of ammonium thiocyanate solution and 20 ml of pyridine, and stir. A dark-blue thiocyanate complex of vanadium is formed. Add 100 ml of chloroform. The organic layer becomes dark blue.

Experiment 167. Extraction of the Permanganate Ion in the Form of Its Tetraphenyl Arsonium Salt

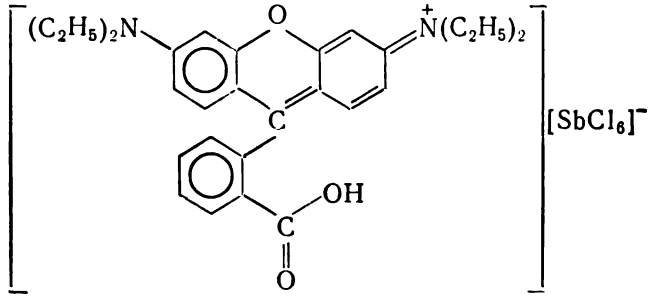
In the presence of tetraphenyl arsonium cations, permanganate ions are extracted with chloroform in the form of the salt $(C_6H_5)_4As^+MnO_4^-$.

Reagents
Potassium permanganate, 0.01 per cent solution.
Tetraphenyl arsonium chloride.
Chloroform.

Procedure. In a cylinder, put 5 ml of potassium permanganate solution and 200 ml of water. At the lecture, add 1 g of tetraphenyl arsonium chloride and 100 ml of chloroform, and stir. The organic layer becomes pink.

Experiment 168. Extraction of the Ion Associate of the Chloride Complex of Antimony with Rhodamine B

Hexachloroantimonate ions $[SbCl_6]^-$ form with the cations of rhodamine B, a red-violet ion associate, which is extracted with organic solvents



The extraction of the ion associate with benzene and toluene is due to the nature of a molecule of rhodamine B, while its extraction with chloroform, amyl alcohol and diisopropyl ether is due to the coordination of solvent molecules [39].

Reagents

Antimonic chloride, 0.1 per cent solution in 6 *M* hydrochloric acid solution.
Rhodamine B, 0.1 per cent solution.
Benzene.
Hydrochloric acid, 2 *M* solution.

Procedure. In a cylinder, put 30 ml of antimony chloride solution and 150 ml of 2 *M* hydrochloric acid solution. At the lecture, add 5 ml of rhodamine B solution and 100 ml of benzene, and stir. The organic layer becomes violet-red.

VOLATILITY OF METAL CHELATES

On heating, many chelates are capable of being sublimated without decomposition (for example, nickel dimethylglyoximate and metal 8-hydroxyquinolinates); this shows the strength of the bonds in the compounds. It should be emphasized that sublimation leads to losses

when making gravimetric determinations. The data of thermogravimetric analysis are used to establish the permissible temperature of drying (ignition) the precipitates

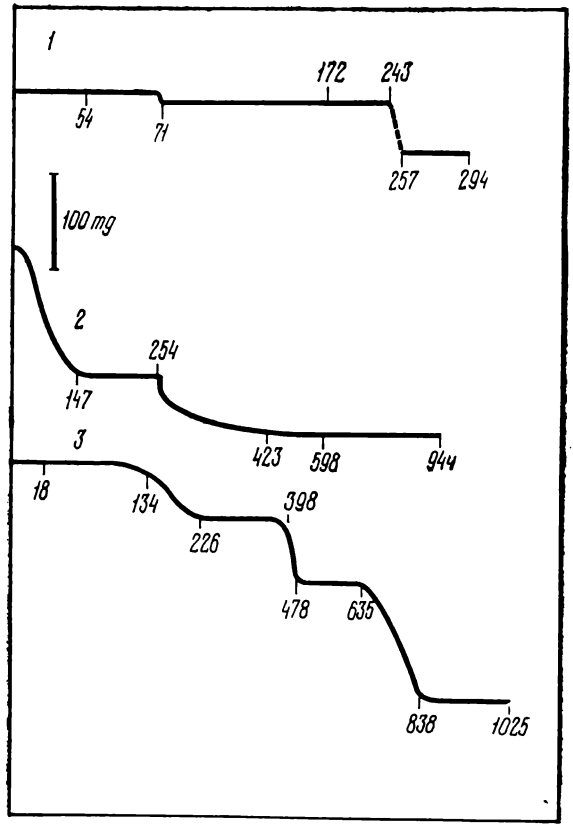


Fig. X-5. Thermogravigrams of:
1 — nickel dimethylglyoximate; *2* — cobalt α-nirtoso-β-naphtholate; *3* — calcium oxalate

of chelate compounds. The audience may be shown illustrations with thermogravigrams (Fig X-5).

Experiment 169. Sublimation of Nickel Dimethylglyoximate

Procedure. Put 2-3 g of dry nickel dimethylglyoximate on the bottom of a dry test tube, made of heat-resistant glass, that has a length of 30 cm and a diameter of 3 cm.

Heat the bottom of the test tube with a burner flame. A pink deposit of nickel dimethylglyoximate is formed on the cold walls of the test tube. A sublimate may be prepared beforehand, and a closed test tube with an appropriate label may be presented to the audience.

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CHAPTER XI

Preparation of a substance for analysis

A homogeneous substance and likewise a heterogeneous substance may be an object of analysis. Usually, it is necessary to use heterogeneous substances in work, and their average composition must be determined. Therefore, an important task of an analyst is to select a representative average sample [1-5].

SAMPLING

Sampling consists of several operations: grinding, sifting and quartering. Every operation affects the accurate selection of an average sample and, consequently, a representative sample.

In reading a lecture, some samples for analysis should be shown, placing homogeneous substances (calcite, feldspar, steel, bronze) and heterogeneous substances (granite, ore, sand) on the demonstration table.

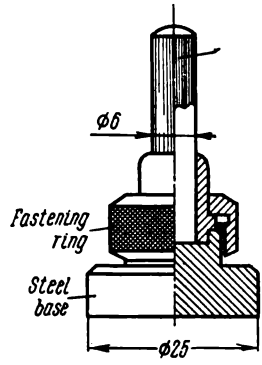

Fig. XI-1. Abich mortar

Substances are ground in several stages. The primary sample, which weighs up to 100 kg, is coarsely ground in special mills of different type. A laboratory sample, which weighs 25-100 g, is ground in mortars. A set of different mortars should be shown: the steel Abich mortar for coarse grinding, porcelain and agate mortars for fine grinding, and a quartz mortar for grinding especially pure substances (Figs. XI-1 and XI-2).

A ground sample is passed through a sieve with openings of different diameter. To preclude the contamination of the sample with metal, especially pure substances are passed through nylon sieves.

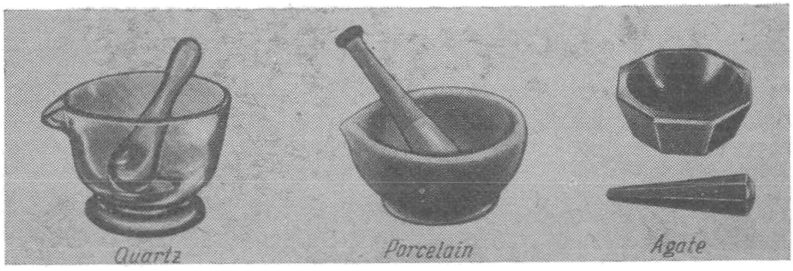

Fig. XI-2. Mortars

A sample of a homogeneous substance, such as a metal or an alloy, is taken by drilling out a shaving in a definite order. A metal or alloy bar with drilled out holes

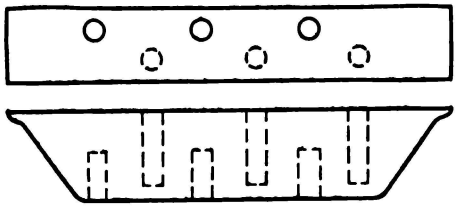

Fig. XI-3. Sampling a metal and an alloy by drilling

(Fig. XI-3) may be presented, and a jar with a shaving of a sample and another jar with a shaving of a standard sample of steel or alloy may be put next to it.

The average sample of a heterogeneous substance is taken by quartering [3].

Experiment 170. Sampling of Sand by Quartering

Pour 70-100 g of bank sand prepared beforehand from a weighing bottle on a sheet of plexiglas or cellophane whose dimensions are 25 cm × 30 cm. Press cone I that

is formed (Fig. XI-4) with a plexiglas plate of 10 cm × × 10 cm. A truncated cone II is produced. Divide the cone into four parts III with a piece of paper that is folded at an angle of 90°, and separate the two opposite sectors, joining them into a new cone IV. Note that the division should be continued until the amount of a sample needed for analysis is obtained.

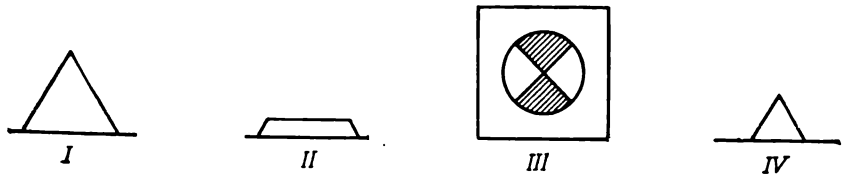

Fig. XI-4. Sampling by quartering

It should also be emphasized that the division of the sample into four parts is not obligatory; a sample may be selected with a spatula, say in a checkered order.

PHASE ANALYSIS

In analyzing heterogeneous substances, such as rocks, ores and sand, it is necessary to know not only the average, general element composition, but also the composition of separate phases and inclusions [3, 5]. In this case, after the sample is ground, the phases are separated before the decomposition or dissolution of the sample by extracting a magnetic fraction with a magnet (magnetic separation) or by other methods.

Experiment 171. Separation of Magnetite by an Ordinary Magnet

Some minerals have more or less permanent magnetic properties. The magnetic properties of other minerals, which are an isomorphous mixture of magnesia and ferriferrous silicates, change as the chemical composition and molecular structure change. Inclusions also exert strong influence.

A scale of magnetizability where the magnetizability of pure iron is taken as 100,000 may be presented:

Magnetite	64,000	Orthite	53
Ilmenite	20-12,000	Hematite	43
Pyrite	60	Limonite	22
Magnetite-hematite .	2,400	Chromite	140
Olivine (69% of FeO)	250	Siderite	290-120
Olivine (15% of FeO)	60	Granate	300-100

Minerals of different magnetizability may be separated by an electromagnet.

Procedure. Mix quartz sand and ground magnetite of approximately the same dispersion degree (the particle diameter being about 1 mm) in the ratio 10 : 1. Pour the mixture evenly on a sheet of white paper and pass a horseshoe magnet over the layer. Remove the attracted particles from the magnet. Two heaps are produced: the light heap is quartz sand and the dark heap is magnetite.

Experiment 172. Separation of Minerals According to Specific Weight by a Heavy Liquid

Phases may be separated by using the difference in the specific weight of minerals and by selecting a liquid with

Table

SPECIFIC WEIGHT OF SOME MINERALS AND HEAVY LIQUIDS

Name and formula	Colour	Specific weight, g/cm³
Minerals		
Sulphur S	Yellow	2.0
Gypsum $CaSO_4 \cdot 2H_2O$	Colourless	2.3
Calcite $CaCO_3$	Colourless	2.7
Liquids		
Bromoform $CHBr_3$	Colourless	2,9
Thoulet solution $K_2[HgI_4]$	Colourless	3.0
Minerals		
Barite $BaSO_4$	Colourless	4.3
Magnetite Fe_3O_4	Black	5.0
Wolframite $(Fe, Mn)WO_4$	Black	7.2

certain density: minerals that are lighter than the liquid float, and minerals that are heavier sink [3]. The audience should be shown a table of specific weights of some minerals and liquids (see the table).

Reagents

Potassium mercurotetraiodide $K_2[HgI_4]$, saturated solution (Thoulet solution).

Bromoform. In the course of time, bromoform becomes dark due to decomposition with the formation of bromine. To remove bromine, the liquid is shaken in separatory funnel first with 1 per cent sodium sulphite solution and then with 1 *M* alkaline solution.

Minerals that are lighter and heavier than the liquid, such as gypsum and magnetite or wolframite.

Procedure. In three cylinders, put a Thoulet solution or bromoform. In one cylinder, put pieces (with a diameter of 2-4 mm) of a light-coloured mineral that is lighter than the liquid (gypsum). The mineral floats on the surface. In another cylinder, put pieces of a dark mineral that is heavier than the liquid (wolframite, magnetite). The mineral sinks. In the third cylinder, put a mixture of a light-coloured light mineral and a dark heavy mineral. The minerals are separated.

To make the experiment illustrative, it is important to select minerals with a contrasting colour. After the experiment, filter off the liquid and keep it in dark bottles.

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CHAPTER XII

Methods of separation of elements

Most methods of separation are based on the distribution of a substance between two phases: a solid and a liquid (methods of precipitation, coprecipitation, crystallization, adsorption and ion exchange), a liquid and a gas or vapour (distillation), two liquids (extraction), and a solid and a gas (adsorption, sublimation). Separation is possible also in a homogeneous medium (diffusion, ion transfer) [1-11].

In modern analysis, many operations of separation are automatic.

PRECIPITATION AND COPRECIPITATION AS A METHOD OF SEPARATING AND CONCENTRATING ELEMENTS

Methods of separation by precipitation are widely used in analysis, notwithstanding the long and labour-consuming operations. Precipitation is carried out at a pH-value that is controlled (see Experiments 13, 161) by complex formation (see Experiments 13, 50), oxidation or reduction of one group of the ions that is being separated (see Experiment 49), and also by the use of various solvents [2-8, 10, 11]. The solubility values of sodium perchlorates and potassium perchlorates in different solvents are given below (in percentage):

	$NaClO_4$	$KClO_4$
Water	114	2.04
Acetone	36	0.12
Methanol	36	0.08
Ethanol	11	0.009
n-Butanol	1.5	0.003

The importance of organic reagents should be especially emphasized (see Chapter X).

The coprecipitation method is effective in separating small amounts of elements, i.e., microelements (see p. 138). An illustration of microelement coprecipitation by isomorphous displacement may be shown (Fig. XII-1). As the illustration shows, when the values of the homogeneous

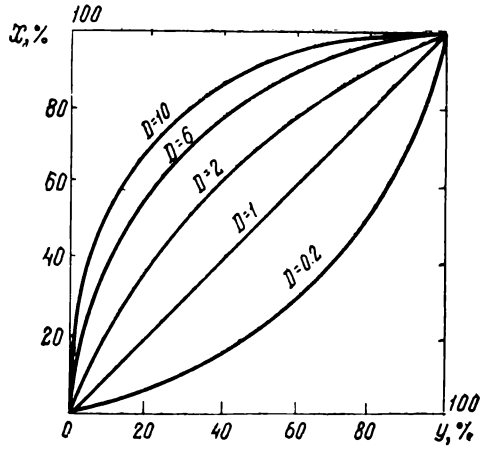


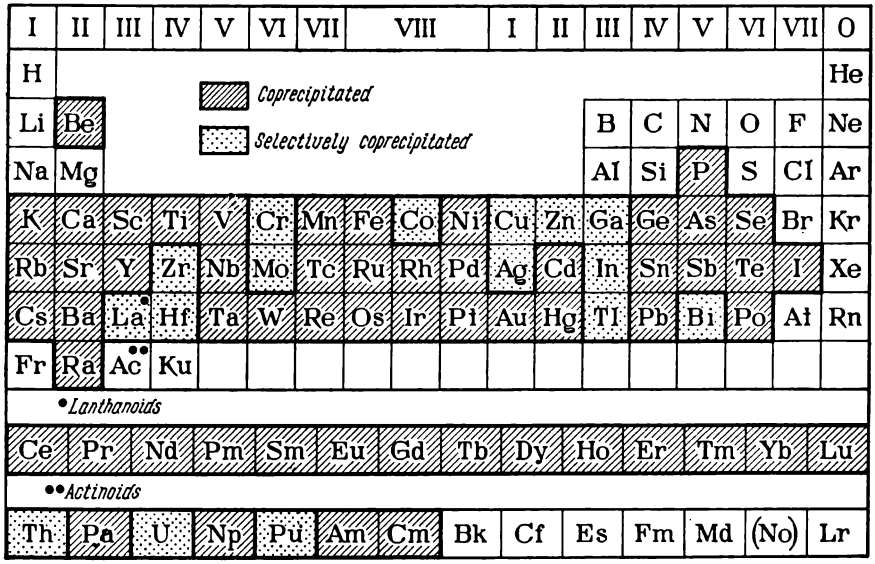
Fig. XII-1. Amount of coprecipitated microelement at different values of the distribution coefficient D

distribution coefficient D are greater than unity, the precipitate is enriched with a microelement; when the values of D are less than unity, the solution is enriched:

$$D = \frac{x(1-y)}{y(1-x)}$$

where x = quantity of a microelement in the precipitate;
y = quantity of a macrocomponent in the precipitate;
$1-x$ = quantity of a microelement in the solution;
$1-y$ = quantity of a macrocomponent in the solution.

Coprecipitation with organic coprecipitants may be shown by using Mendeleyev's periodic table [12].


I II III IV V VI VII VIII I II III IV V VI VII 0
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Ac Ku
Coprecipitated
Selectively coprecipitated
•Lanthanoids
Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
••Actinoids
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md (No) Lr

Wide use is made of the cementation method, which is based on the displacement of a less active metal with a more active one from a salt in a solution [13].

Cementing metal	Metal being separated
Mg	Cd, Ni, Pb, Bi, Cu, Hg, Ag
Fe	Co, Ni, Pb, Sb, Bi, Cu
Zn	Sn, Pb, Cu, Hg
Cd	Sn, Pb, Sb, Hg, Ag

The classical arrangement of the systematic course of analysis of cations with the utilization of hydrogen sulphide is the basis of the study of qualitative analysis and is dealt with at length in all textbooks. Therefore, a lecturer must as a rule devote sufficient attention to equilibrium in hydrogen sulphide solutions, properties of sulphides and possible complications during analysis. Since sulphide ion concentration is determined to a considerable extent by hydrogen ion concentration

$$[S^{2-}] = \frac{C_{H_2S}}{1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1 K_2}}$$

it is expedient to show a diagram of distribution of H_2S, HS^- and S^{2-}, depending on the pH of the solution (see Fig. IV-2, *b*).

Properties of Metal Sulphides

Metal sulphides are compounds with a complex structure. The structure and composition of precipitates usually depend on the ratio of reactant concentrations, the precipitation rate, temperature and other conditions; therefore, almost all sulphides exist in the form of modifications, which differ from one another by their properties (colour and solubility). Moreover, they rarely form strictly stoichiometric compounds precipitating from a solution. Some sulphides, such as arsenous and arsenic sulphides and antimonous and antimonic sulphides, have an amorphous structure and are polymer formations. Sulphide precipitates have a well developed surface, and this promotes considerable coprecipitation of other cations. Many sulphides have a specific colour, and this is used to detect metal ions after their separation (see Experiment 12).

When reading a lecture on hydrogen sulphide precipitation, use may also be made of Experiments 89 and 91, which illustrate the formation and stabilization of sulphide sols, and also Experiment 61, which shows comparative sulphide solubility.

Note. Experiments with hydrogen sulphide may be carried out only on condition there is a hood in the auditorium or on the lecture table.

Experiment 173. Sulphide Modifications

There is no single viewpoint as to the nature of sulphide precipitate modifications. The differences may be in the structure of a crystal lattice and in the degree of hydration or degree of oxidation of the metal. For example, manganese sulphide of pink colour ($-\log K_{sp} = 9.6$) is a hydrated form; on boiling, it changes to a modification of green colour, which is a crystal anhydrous sulphide ($-\log K_{sp} = 12.6$).

It is known that when sulphide ions are added to cobaltous and nickel salts, black sulphides in the α-form are

obtained, and when they are heated in the air, less soluble β- and γ-modifications are formed [14]; it may be possible that, in this case, sulphides are oxidized to Ni(OH)S and Co(OH)S:

$$-\log K_{sp_{CoS\ (\alpha)}} = 20.4$$

$$-\log K_{sp_{CoS\ (\beta)}} = 24.7$$

$$-\log K_{sp_{NiS\ (\alpha)}} = 18.5$$

$$-\log K_{sp_{NiS\ (\gamma)}} = 25.7$$

Antimony (III) also forms two sulphide modifications, which are orange and black and which differ from each other apparently by their structure.

When hydrogen sulphide is passed through a mercuric chloride solution, faint-coloured compounds are formed, being double salts, such as $2HgS \cdot HgCl_2$. On heating, black mercury sulphide turns, under the action of alkaline polysulphides, into a red form that is identical with the cinnabar mineral.

There is much evidence to the effect that α-modifications of metal sulphides are hydrosulphides $M(HS)_n$, which in the course of time become normal sulphides.

To demonstrate sulphide modifications, it is convenient to use precipitates of different colour.

Reagents

Manganous, antimonous and mercuric chlorides, 1 per cent solutions.
Ammonium chloride.
Ammonia, 25 per cent solution.
Hydrogen sulphide, gas.

Procedure. Prepare different sulphide modifications beforehand and put them in tightly-stoppered cylinders with labels. α-Modifications are prepared by passing hydrogen sulphide through salt solutions: pink manganese sulphide is produced at pH = 8, and orange antimony sulphide and black mercury sulphide are produced in 0.5 *N* hydrochloric acid solution.

To prepare β-modifications of green manganese sulphide, put 100 ml of manganese chloride solution, 10 g of solid

ammonium chloride and 50 ml of ammonia solution in a conical flask, pass through hydrogen sulphide until saturation, and heat the pink precipitate in a sand bath for 3-4 hours.

To prepare a black modification of antimony sulphide, precipitate orange sulphide in 4 *M* hydrochloric acid solution and heat the precipitate for several hours.

A light-grey mixed mercury sulphide may be prepared by adding a small amount of hydrogen sulphide solution to a strongly acid hydrochloric solution of mercury chloride.

To demonstrate the red modification of mercury sulphide, the cinnabar mineral may be used.

Experiment 174. Precipitation of Cobalt Sulphides and Nickel Sulphides in the Presence of Pyridine

When hydrogen sulphide is passed through a solution of a nickel salt or a cobaltous salt, a black flaky cryptocrystalline precipitate is formed. However, if precipitation is carried out in the presence of pyridine, a precipitate is produced in the form of crystals which are well noticeable by the naked eye and which rapidly settle to the bottom of the vessel. This is due to the slow formation of sulphide crystals as the complex ion is dissociated [15]:

$$[NiPy_4]^{2+} \rightleftarrows Ni^{2+} + 4Py$$
$$Ni^{2+} + S^{2-} \rightleftarrows NiS$$

Reagents

Nickelous chloride, 1 per cent solution.
Pyridine, 20 per cent solution.
Hydrochloric acid, concentrated.
Hydrogen sulphide, gas.
Methyl red, 0.1 per cent ethanol solution.

Procedure. In a conical 0.5-litre flask, put 10 ml of nickel chloride solution and 300 ml of water. At the lecture, divide the solution into two parts. To one part, add 0.5 ml of hydrochloric acid solution, several drops of methyl red and pyridine solution until a yellow colour ap-

pears, and then another 5 ml of excess pyridine. Heat the solution to boiling and pass hydrogen sulphide through it for 15 minutes. A brilliant crystal precipitate of nickel sulphide is formed. At the same time, having heated the other part of the nickel salt solution to boiling, pass hydrogen sulphide through it. An amorphous precipitate of nickel sulphide is formed.

Precipitation and Dissolution of Metal Sulphides

The dissolution of metal sulphides increases as the sulphide ion concentration decreases. The sulphide ion concentration may be reduced by binding sulphide ions into poorly-dissociated hydrosulphuric acid, and by forming thio ions of amphoteric elements and changing the degree of oxidation of sulphur. To calculate the solubility of metal sulphides, use should be made of the conditional solubility product (Chapter VI) and the standard oxidation-reduction potential of the S/MS system (see Chapter VIII):

$$K_{sp}^{con} = K_{sp}^{t} \frac{1}{\alpha_1}$$

$$\frac{1}{\alpha_1} = 1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1 \cdot K_2}$$

$$E^{\circ}_{S/MS} = E^{\circ}_{S/S^{2-}} - \frac{RT}{2F} \ln K_{sp}^{t}$$

where K_{sp}^{t} = table value of the solubility product of metal sulphide;

E° = standard potential of the S/S^{2-} pair.

If, together with the reaction of metal sulphide precipitation, a side complex-formation reaction involving metal ion occurs, the equilibrium concentration of metal decreases. In this case, the solubility of sulphide should be calculated on the basis of the conditional solubility product:

$$K_{sp}^{con} = K_{sp}^{t} \frac{1}{\alpha_2}$$

$$\frac{1}{\alpha_2} = \frac{c_M}{[M]} = 1 + \sum_{1}^{N} \beta_n a^n$$

where β_n = overall stability constant of the complex;
a = equilibrium concentration of the complexing agent (see p. 129).

On the formation of strong complexes, the conditional solubility product of sulphide is so great that the formation of metal sulphide is impossible.

Experiment 175. Separation of Copper and Cadmium in the Form of Their Sulphides in the Presence of Thiourea

Cupric ions are reduced by thiourea, forming cuprous ions, which produce strong complex compounds with a reagent excess $[Cu(SCN_2H_4)_2]^+$, $[Cu(SCN_2H_4)_3]^+$ and $[Cu(SCN_2H_4)_4]^+$. A precipitate of only cadmium sulphide is formed when hydrogen sulphide is passed through a solution of copper and cadmium salts in the presence of thiourea.

Reagents
Thiourea, saturated solution.
Cupric sulphate, 1 per cent solution.
Cadmic sulphate, 1 per cent solution.
Hydrochloric acid, 2 *M* solution.
Hydrogen sulphide, saturated solution.

Procedure. In a cylinder, put 10 ml of copper salt solution and the same amount of cadmium salt solution, dilute to 100 ml with water, and add hydrochloric acid solution until pH = 2 ÷ 4. At the lecture, pour the solution into two cylinders. To one cylinder, add 50 ml of hydrogen sulphide solution. A mixture of black sulphides precipitates. To the other cylinder, add 100 ml of thiourea solution and 50 ml of hydrogen sulphide solution. Only a yellow precipitate of cadmium sulphide is formed.

Experiment 176. Prevention of the Formation of Stannic Sulphide in the Presence of Fluoride Ions

The stannic ion forms complex compounds with such fluoride ion as $[SnF_6]^{2-}$. Therefore, tin sulphide is not precipitated when hydrogen sulphide is passed through in the

presence of an excess of fluoride ions. This property may be used to separate tin from the elements which do not form fluoride complexes.

Reagents

Stannic chloride, 0.1 per cent solution in 2 *M* hydrochloric acid solution.
Ammonium fluoride, saturated solution.
Hydrogen sulphide, saturated solution.

Procedure. In a cylinder, put 400 ml of stannic chloride solution. At the lecture, pour the solution into two cylinders. To one cylinder, add hydrogen sulphide solution. A yellow precipitate of tin sulphide is formed. To the other cylinder, add 50 ml of ammonium fluoride solution and hydrogen sulphide solution. A precipitate is not formed.

Experiment 177. Prevention of the Formation of Mercury Sulphide

Mercuric ions form with iodide ions, the strong complexes $[HgI]^+$, $[HgI_2]$, $[HgI_3]^-$ and $[HgI_4]^{2-}$ (see Experiment 67), $\log \beta_4 = 29.8$. Notwithstanding the poor solubility of mercury sulphide ($-\log K_{sp} = 51.8$) in an acid medium in the presence of iodide ions, a precipitate of mercury sulphide is not formed.

Reagents

Mercuric nitrate, 1 per cent solution in 0,1 *N* nitric acid solution.
Potassium iodide, saturated solution.
Hydrogen sulphide, saturated solution.
Hydrochloric acid, 2 *M* solution.

Procedure. In a cylinder, put 10 ml of mercury nitrate solution and 300 ml of water, and acidify with 20 ml of hydrochloric acid solution. At the lecture, divide the solution into two parts. To one part, add hydrogen sulphide solution. A black precipitate of mercury sulphide is formed. To the other, add 50 ml of potassium iodide solution; a red precipitate of mercury iodide is formed and dissolved. Then, add hydrogen sulphide solution. A precipitate is not formed.

Experiment 178. Dissolution of Lead Sulphide in the Presence of Hydrogen Peroxide

Lead sulphide is highly soluble in an acid medium on an addition of hydrogen peroxide, which oxidizes the sulphide ion

$$PbS + H_2O_2 + H_2SO_4 \rightleftarrows PbSO_4 + S + 2H_2O$$

The standard oxidation-reduction potential of the system H_2O_2, $2H^+/2H_2O$ is 1.77 V, and it is greater than the standard oxidation-reduction potential of the system S/PbS, H^+

$$E^\circ_{S/PbS,\,H^+} = 0.14 - \frac{0.059}{2} \log K_{sp_{PbS}} = 0.93V$$

$$-\log K_{sp_{PbS}} = 27$$

Hence, the reaction is virtually displaced to the right.

Lead sulphate dissolves when heated in sodium hydroxide solutions due to the formation of hydroxo complexes

$$PbSO_4 + 4NaOH \rightleftarrows Na_2[Pb(OH)_4] + Na_2SO_4$$

Reagents

Lead (II) acetate, 1 per cent solution.
Hydrogen peroxide, 3 per cent solution.
Hydrogen sulphide, saturated solution.
Sulphuric acid, 1 *M* solution.
Sodium hydroxide, 20 per cent solution.

Procedure. Prepare a lead sulphide precipitate in a cylinder beforehand by adding hydrogen sulphide solution to lead acetate solution. At the lecture, agitate the precipitate, add 50 ml of sulphuric acid solution and 30-50 ml of hydrogen peroxide solution, and stir. The black precipitate of lead sulphide is turned into a white precipitate of lead sulphate. Add 100 ml of sodium hydroxide solution. The precipitate of lead sulphate is dissolved.

Experiment 179. Dissolution of Copper Sulphide in an Ammonia Medium in the Presence of Hydrogen Peroxide

The dissolution of copper sulphide under the action of hydrogen peroxide in an ammonia solution is due to the oxidation of the sulphide ion and the simultaneous forma-

tion of the complex ion $[Cu(NH_3)_4]^{2+}$:

$$CuS + H_2O_2 + 4NH_3 \rightleftarrows [Cu(NH_3)_4]^{2+} + S + 2OH^-$$

$$E^\circ_{H_2O_2/2OH^-} = 0.88 \text{ V}$$

$$E^\circ_{S/CuS,\,NH_3} = -0.48 - \frac{0.059}{2} \log K_{sp_{CuS}} \cdot \beta_4 = 0.21 \text{V}$$

For $[Cu(NH_3)_4]^{2+}$, $\log \beta_4 = 12.03$; $-\log K_{sp_{CuS}} = 35.2$

Hence, the reaction is virtually displaced to the right.

Reagents

Cupric sulphate, 1 per cent solution.
Hydrogen sulphide, gas.
Ammonia, 25 per cent solution.
Hydrogen peroxide, 3 per cent solution.

Procedure. Prepare a precipitate of copper sulphide in a cylinder beforehand by passing hydrogen sulphide through a copper sulphate solution. At the lecture, agitate the precipitate and add 20 ml of ammonia solution and 30 ml of hydrogen peroxide solution. A black precipitate of copper sulphide is dissolved and a dark blue complex of copper ammoniate is formed.

CHROMATOGRAPHIC METHODS OF SEPARATION

Chromatography is a method of multistage separation of mixtures of several components that is based on the difference in the distribution coefficients of the components of a mixture between the mobile and the stationary phases.

Chromatography is classified into partition, ion-exchange, adsorption and other types [16].

Ion Exchange Chromatography

Ion exchange is characterized by the following equilibrium:

$$RH + M^+ \rightleftarrows RM + H^+$$
$$ROH + A^- \rightleftarrows RA + OH^-$$

where RH and ROH = ion exchangers. Solid insoluble substances containing positively or negatively charged

groups are used as ion exchangers. At present, synthetic organic ion exchangers (ion exchange resins) and insoluble high-polymer acids and bases are mainly used in practice.

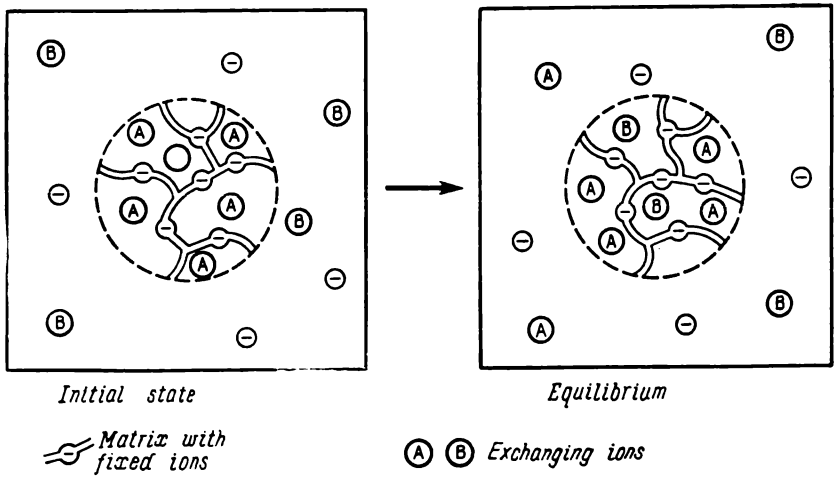


Fig. XII-2. An illustration of ion exchange between an ion exchanger and a solution

At the lecture, the listeners may be shown an illustration of ion exchange between an ion exchanger and a solution (Fig. XII-2). On the demonstration table, put a set

Table

PROPERTIES OF SOME ION EXCHANGERS

Brand	Functional groups	Exchange capacity, mg-equiv/g
Cation exchangers		
КУ-1	$-SO_3H$, $-OH$	4-5
КУ-2	$-SO_3H$	4-5
СВД	$-SO_3H$	4
СБС	$-SO_3H$	3
КБ-4	$-COOH$	10
Anion exchangers		
АВ-17	$-\overset{+}{N}(CH_3)_2$	4
Н-О	$=NH$, $\equiv N$	4
АН-2Ф	$=NH$, $\equiv N$	10
АН-1	$-NH_2$, $=NH$	4

of ion exchangers in jars with the labels: КУ-1, КУ-2, СДВ, СБС, КБ-4, АВ-17, Н-0, АН-1, and so forth. The characteristics of ion exchangers are given in the table (p. 289).

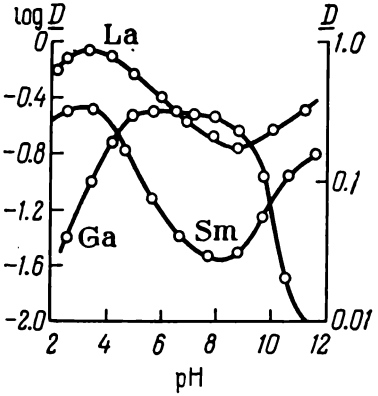


Fig. XII-3. Coefficients of distribution ($\underline{D}$) of the ions of lanthanum, samarium and gallium between a monofunctional iminodiacetic resin and 0.1 M nitrilotriacetic acid in conformity with the pH

The separation of ions with similar properties by the chromatographic method is based on the different stability

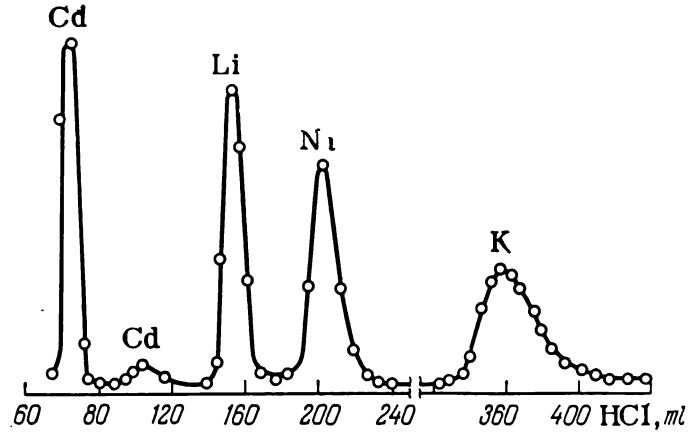


Fig. XII-4. Separation of the ions of cadmium, lithium, sodium and potassium by the ion-exchange method. The ions are washed out with 0.7 *N* hydrochloric acid at a rate of 0.55 cm per minute

of the complexes of these ions in conformity with the pH (Fig. XII-3) [17]. The listeners may be shown a chromatogram illustrating the separation of the ions of cadmium, lithium, sodium and potassium (Fig. XII-4).

It should be emphasized that ion exchange resins are widely used for concentrating traces from large volumes [18].

Experiment 180. Separation of Iron and Aluminium Ions by Ion Exchange

The separation of iron and aluminium ions is based on the formation of the complex thiocyanate ion of iron, which is sorbed with an anion exchanger.

Equipment and Reagents

Chromatographic column, which is filled with the anion exchanger AB-17 in the OH^--form (Fig. I-7).
Ferric chloride, 1 per cent solution in 0.01 *N* hydrochloric acid solution.
Aluminium chloride, 1 per cent solution.
Ammonium thiocyanate, 5 per cent solution.
Alizarin S, 0.1 per cent ethanol solution.
Ammonia, 2 *M* solution.

Procedure. In a conical flask, prepare a mixture consisting of 1 ml of iron chloride solution, 10 ml of aluminium chloride solution and 30 ml of water. At the lecture, add 10 ml of ammonium thiocyanate solution. Pass the red solution obtained through the column, collecting the outgoing colourless liquid in an empty conical flask. To the colourless liquid, add 5 ml of alizarin S solution and 5 ml of ammonia solution. Red aluminium-alizarin lacquer is obtained.

Partition Chromatography

Partition chromatography is based on the difference in the distribution coefficients of substances, which are being separated, between two immiscible liquid phases: mobile and stationary liquid phases. The stationary liquid phase is firmly retained on the surface of an inert solid support, such as an aluminium oxide or teflon, paper, and so forth [19].

Paper may be represented as the inert solid support of the stationary aqueous phase. When a solvent passes through a region of paper that contains a dissolved substance, the substance is distributed between a mobile organic solvent and a stationary aqueous phase. Hence, a part of the substance passes over to the organic phase. When the mobile solvent reaches the region of paper that does not have the dissolved substance, redistribution again occurs. This time, the substance passes from the organic phase to the aqueous phase, which is fixed on paper. The movement of the band (zone) of the solute is described by the quantity R_f:

$$R_f = \frac{\text{velocity of the zone}}{\text{velocity of the solvent front}}$$

The quantity R_f depends on the nature of the support, the experiment techniques, temperature and other factors, and it should not depend on the concentration of a substance being determined and on the presence of other components.

Experiment 181. Separation of the Ions of Copper, Bismuth and Cadmium by Paper Chromatography

About 40 minutes is required for the given experiment; therefore, ions should be separated beforehand and, at the lecture, only the zones occupied by a certain ion should be shown.

Equipment and Reagents

Cylinder with a cap having a hook (see Fig. VII-5).
Chromatographic paper.
Solvent, a mixture of 40 per cent of tertiary butanol, 40 per cent of acetone, 11 per cent of water, 4.5 per cent of 6 *M* nitric acid solution and 4.5 per cent of acetylacetone.
Potassium ferrocyanide, 1 per cent solution.
Sodium sulphide, 1 per cent solution.
Solution of potassium iodide and 8-hydroxyquinoline. Two grams of 8-hydroxyquinoline and 4 ml of concentrated hydrochloric acid are mixed together, and then

the solution is diluted to 100 ml with water and 2 g of potassium iodide are added.

Bismuthous, cupric and cadmic nitrates, 1 per cent solutions in 1 *M* nitric acid solution.

Procedure. Draw a starting line with a pencil 2 cm away from the edge of a paper strip. On the starting line, draw a circle with a diameter of 5-7 cm. Deposit a drop of the solution being studied in the centre of the circle with a capillary tube (not dropwise, but by pressing the capillary tube to the paper) so that the spot would not spread outside the boundary of the marked circle. The smaller the spot, the clearer is the chromatogram. Dry the spot a little over an electric heater and repeat the operation 2-3 times. Pour the solvent into a cylinder without topping the 0.5-1 cm level. Lower the strip having a deposited drop into the chamber without immersing the drop in the solvent. Close the chamber with a cap. In 30 minutes, take out the paper strip and carefully dry it a little in the air (not over a burner flame!). The cations are arranged in the following order: bismuth is at the front line of the solvent, copper is somewhat lower, and cadmium is above the starting line.

To develop the chromatogram, pass a capillary tube with a mixture of 8-hydroxyquinoline and potassium iodide along the front line; in this case, a bright orange band of the slightly soluble compound $[C_9H_8NO][BiI_4]$ appears. Then, pass a capillary tube with a potassium ferrocyanide solution somewhat below the front line; in this case, a brown-violet band of copper ferrocyanide appears. Pass a capillary tube with a sodium sulphide solution over the starting line. A yellow band of cadmium sulphide is formed.

Precipitation Chromatography

Precipitation chromatography is based on the different solubility of precipitates prepared as a result of a reaction between the ions being separated and a precipitant, which is in the column [20, 21]. A precipitant is used in a mixture with a support. The latter is an insoluble substance, and it is indifferent to the precipitant.

Experiment 182. Separation of the Ions of Silver, Mercury and Lead

The ions of silver, mercury and lead may be detected in the form of iodides by using aluminium oxide as a support and potassium iodide as a precipitant.

Equipment and Reagents

Chromatographic column, which is filled with aluminium oxide and potassium iodide (0.5 mg-equiv per gram of a support).

Nitrates of silver, mercury (II) and lead, 0.01 per cent solutions.

Procedure. Fix the chromatographic column in a test tube and put it in a Bunsen flask, which is connected with a water-jet pump. Prepare a mixture containing 1 ml of silver nitrate solution, 1 ml of mercuric nitrate solution and the same amount of lead nitrate solution, and 20 ml of water. Pass the mixture through the column and wash it with water. Coloured zones are formed: the upper zone is yellow silver iodide, the central zone is orange mercury iodide, and the lower zone is yellow lead iodide.

SOLVENT EXTRACTION METHODS OF SEPARATION

Efficiency, simple procedure, rapid attainment of equilibrium and high selectivity make the extraction method one of the most common methods of separating substances [22-24].

The extraction of different compounds has been examined earlier: chelate compounds, see Experiments 60, 164, 165; inorganic molecules with covalent bonds, see Experiments 7, 57; metal halo acids, see Experiments 6, 58, 59, 141; ion associates, see Experiments 167, 168; mixed complexes, see Experiments 129, 130.

It should be noted that extraction systems are very diverse. The number of extracting agents used in analysis is continually growing.

The effectiveness of extraction as a method of separation may be shown by taking the example of separation of

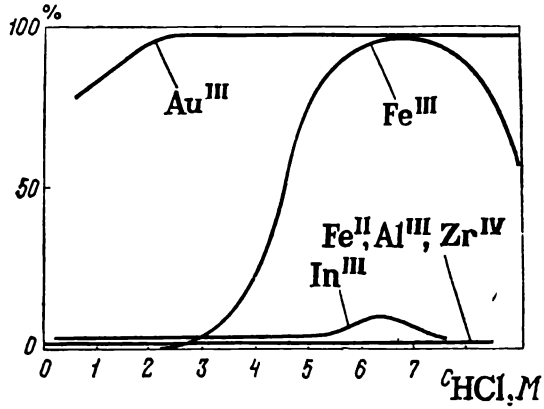


Fig. XII-5. Separation of elements by the extraction of chloride complexes by diethyl ether

such elements as iron (III), iron (II), indium (III), aluminium (III), zirconium (IV) and gold (III) (Fig. XII-5).

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CHAPTER XIII

Mendeleyev's periodic law and analytical chemistry

A general regularity which unifies the properties of different elements is D. I. Mendeleyev's periodic law. Owing to this law, analytical chemistry is not a casual accumulation of different methods that are isolated and independent of one another, but a single whole in which various methods are organically connected with one another [1-19]. In reading lectures, some general regularities of a change in the properties of elements should be shown by several examples.

An analogy in the properties of elements is observed in the periodic system vertically, i.e., within the limits of a group, and horizontally and diagonally. A change in properties diagonally is very important, having played a great role in the elaboration of many analytical methods. A diagram (Fig. XIII-1) may be illustrated to show an analogy in properties vertically (V—Nb—Ta), horizontally (Zr—Nb—Mo or Hf—Ta—W) and diagonally (Ti—Nb—W or Zr—Ta—U). An analogy in properties makes it difficult to determine an element in the presence of other elements; however, this analogy makes it possible to propose new methods of determination. Hence, a well-known reaction of the molybdenum (V) ion with thiocyanate ions turned out to be analogous to a reaction of the niobium ion with thiocyanate ions, and this has made it possible to elaborate a method of determining the niobium ion in the form of a thiocyanate complex [2]. Elements with similar ionic radii are arranged diagonally. Ions having similar radii may replace one another in compounds, and this may be used for separating small quantities of elements (Chapter VI).

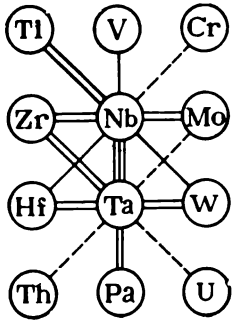


Fig. XIII-1. Similarity of the reactions of elements in conformity with their position in the periodic system

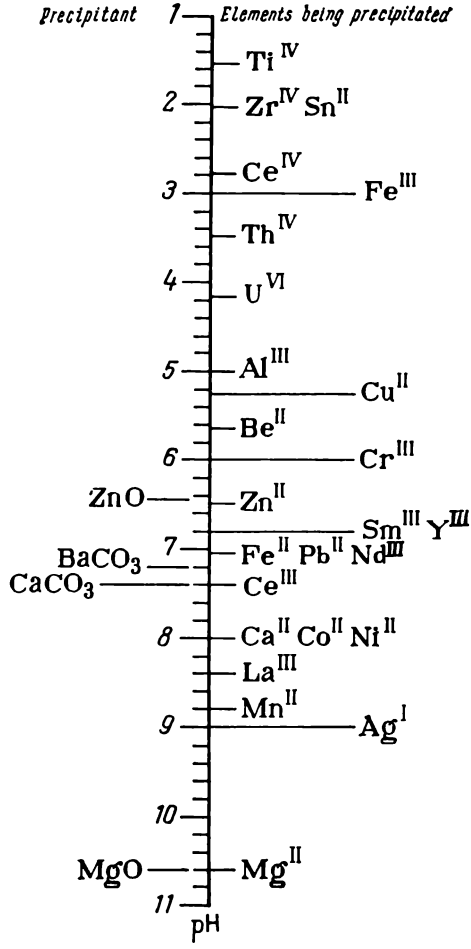
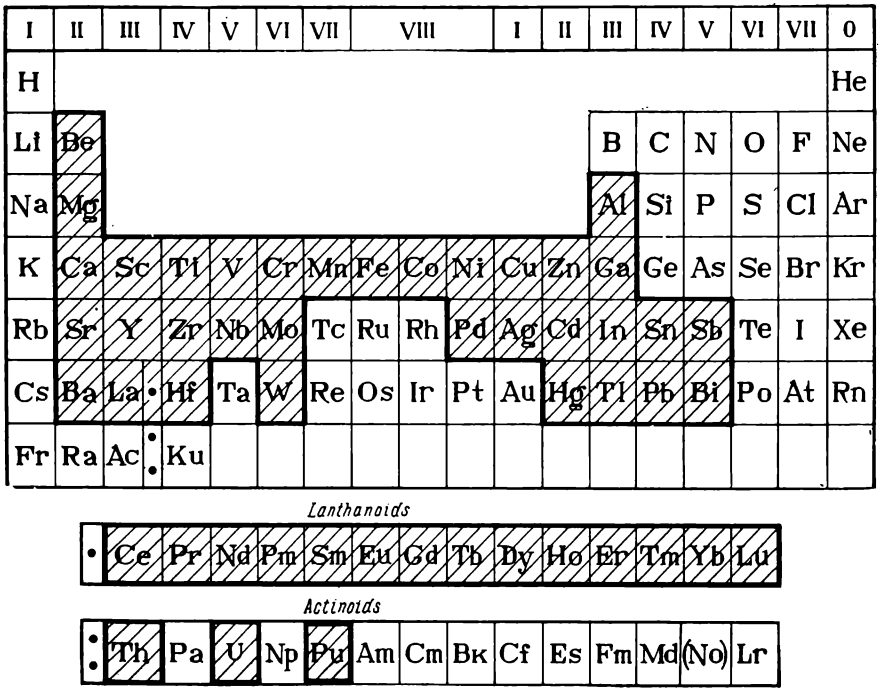


Fig. XIII-2. pH of precipitation of metal hydroxides

The entire periodic system may be divided into "fields" or "blocks", which have elements that possess similar chemical properties used for separating and determining elements. An examination of the electron configuration of atoms and such properties as charge Z and ionic radius r_i, and also ionic potentials Z/r_i and electrostatic characteristic Z^2/r_i makes it possible to estimate many regularities in the chemical properties of elements. Hence, the electron configuration of the atoms of metals determines their interaction with a certain type of ligands. For example, the colour of sulphides and aquo complexes of metals depends on the value of r_i and the electron configuration of an atom. The stability of complex compounds depends on the charge and value of Z/r_i of the central atom. When Z/r_i or Z^2/r_i increases, the pH of precipitation of metal hydroxides decreases (Fig. XIII-2), and the solubility of sulphates of alkali-earth elements increases.

ELEMENTS FORMING COMPLEXES WITH PAN


I II III IV V VI VII VIII I II III IV V VI VII 0
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Ac Ku
Lanthanoids
Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Actinoids
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md (No) Lr

	Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Ionic radius (r_i)	0.34	0.78	1.06	1.27	1.43
Value of Z^2/r_i	11.74	5.12	3.78	3.15	2.80
Solubility of $MeSO_4$, mol/l	~4	~3	$8 \cdot 10^{-3}$	$5 \cdot 10^{-4}$	$1 \cdot 10^{-5}$

Several regularities may be observed if the thermodynamic and kinetic characteristics of a complex-formation reaction are examined in connection with the position of elements in the periodic system. For example, the stability of complexes with EDTA increases with a growth in the charge of metal ion: $Al^{3+} > Mg^{2+} > Na^{+}$; $Sc^{3+} > Ca^{2+} > > K^{+}$. The stability of EDTA complexes of the ions of metals of the subgroups is as a rule higher than that of the ions of metals of the main groups.

ELEMENTS FORMING 8-HYDROXYQUINOLINATES THAT ARE EXTRACTED WITH CHLOROFORM

I	II	III	IV	V	VI	VII	VIII	I	II	III	IV	V	VI	VII	0
H															He
Li	Be									B	C	N	O	F	Ne
Na	Mg									Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Ku														

Lanthanoids

•	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

Actinoids

•	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	(No)	Lr

The correlation between the stability of a complex and the ionic potential of the metal, for a large number of

ligands, makes it possible to ascertain the "natural series" of a change in the stability of complexes (Chapter IX) [8, 9].

The wide utilization of organic reagents has made it possible to ascertain, to a considerable extent, the analogies in the properties of elements (Chapter X) [5-7, 10, 11]. For example, for such reagents as R—OH, there is a dependence between colour reactions and the reactions of element hydrolysis. In a strongly acid medium, reactions with these reagents involve elements which are easily hydrolized: Zr, Hf, Th, Ti, Nb, Ta. Ions of metals of the hydrogen sulphide group react with such reagents as R—SH in an acid medium.

In respect to such reagents as arsenazo III, the origination of colour reactions of elements, and also the value of molar absorptivity, depend on the ionic radii of elements (see the Table) [11].

Table

IONIC RADII r_i OF ELEMENTS AND THE MOLAR ABSORPTIVITIES $\bar{\varepsilon}$ OF THEIR COMPLEXES WITH ARSENAZO III [11]

Me^{II}	r_i^*, Å	$\bar{\varepsilon}\cdot10^{-3}$	Me^{III}	r_i, Å	$\bar{\varepsilon}\cdot10^{-3}$	Me^{IV}	r_i, Å	$\bar{\varepsilon}\cdot10^{-3}$
Be^{2+}	0.31	0	B^{3+}	(0.20)	0	Ge^{4+}	0.55	0
Zn^{2+}	0.56	0	Al^{3+}	0.55	0	Ti^{4+}	0.60	0
Hg^{2+}	0.66	0	Ga^{3+}	(0.65)	0	Sn^{4+}	0.65	0
Mg^{2+}	0.78	0	In^{3+}	(0.95)	0	Hf^{4+}	(0.77)	95
Cd^{2+}	0.99	0	Tl^{3+}	1.05	0	Zr^{4+}	0.80	120
Ca^{2+}	1.05	10	Sc^{3+}	0.81	19	Pu^{4+}	0.93	136
Sr^{2+}	1.17	10	Y^{3+}	0.93	55	Np^{4+}	0.95	100
Ba^{2+}	1.39	10	La^{3+}	1.14	45	U^{4+}	1.02	130
UO_2^{2+}	—	53	Ce^{3+}	1.18	47	Th^{4+}	1.10	130

If this regularity is examined in conformity with the value of Z/r_i, all ions with the value of $Z/r_i \geqslant 46$ form with arsenazo III complexes of green colour, and all ions with the value of $Z/r_i \leqslant 39$ form complexes of dark blue-violet and dark blue colour.

Mendeleyev's table may be shown, indicating the elements that give colour reactions with organic reagents,

such as PAN, sodium dithiocarbaminate and 8-hydroxyquinoline, which are widely used for the photometric determination and the extraction separation of elements.

A considerably larger number of examples may be given; however, there is no need for this. The main task of the lectures is to show by several vivid examples that the periodic system of the elements is an inexhaustible source of new investigations in analytical chemistry.

Experiment 183. Similarity and Difference in the Properties of Ions of Magnesium, Scandium and Zirconium on Interaction with the Phosphate Ion

In analyzing objects of a complex composition (minerals, ores, alloys, and so forth), elements are divided into groups by using the similarity and difference of their ions in connection with the position in the periodic system. The similarity of the properties of elements is manifested according to the subgroups, series and the diagonal. Due to the diagonal similarity, which is determined by the closeness of ionization potentials and electronegativity, such elements as magnesium, scandium and zirconium form slightly soluble phosphates. However, the difference in the charges of ions, and also the different number of the inner shells of electrons, lead to a difference in the properties of their compounds. Magnesium phosphate dissolves in acetic acid, and scandium phosphate in hydrochloric acid, while zirconium phosphate does not dissolve in these acids. These properties of phosphates may be used for separating the given elements.

Reagents

Chlorides of magnesium, scandium and zirconium, 0.1 per cent solutions in 1 *M* hydrochloric acid solution.
Sodium dihydrophosphate, 0.5 per cent solution.
Ammonia, 10 per cent solution.
Sodium acetate, 10 per cent solution.
Acetic acid, 1 *M* solution.
Hydrochloric acid, 4 *M* solution.

Procedure. In a cylinder, put 20 ml of magnesium chloride solution and 5 ml of ammonia solution, in another cylinder, put 20 ml of scandium chloride solution and 50 ml of sodium acetate solution, and in the third cylinder, put 20 ml of zirconium chloride solution. Add 200 ml of water to each cylinder. At the lecture, add 50 ml of sodium dihydrophosphate solution to each cylinder. White precipitates of metal phosphates are formed in all cylinders. To each cylinder, add 30 ml of acetic acid solution. The precipitate in the first cylinder dissolves, while scandium phosphate and zirconium phosphate do not dissolve. Add 30 ml of hydrochloric acid solution to the second cylinder and likewise to the third one. Only scandium phosphate dissolves.

Note. The commonness and difference in the properties of elements according to groups and series may be shown by taking the example of metal sulphides (conditions of the formation of sulphides, and their solubility and colour): ZnS, CdS and HgS; As_2S_3, Sb_2S_3 and Bi_2S_3; FeS, CoS and NiS; CdS, SnS and Sb_2S_3.

Experiment 184. Comparison of the Action of Arsenazo III on the Ions of Magnesium, Aluminium, Zirconium and Thorium

The electronic structure of atoms and ions makes it possible to explain and predict the action of many reagents. If the periodic system is divided into four blocks (*s*-block, *p*-block, *d*-block and *f*-block), the elements of the *d*-block and the *f*-block form complexes. They are likewise characterized by interaction with organic reagents and formation of a large number of coloured compounds. Zirconium and thorium (*d*- and *f*-blocks) form with arsenazo III stable complexes of green colour. Magnesium and aluminium (*s*- and *p*-blocks) do not interact with arsenazo III. The *s*-block has elements in which the *s*-shell is formed above the electron structure of an inert gas; they are alkaline and alkali earth elements. The elements of the *s*-block exhibit the least tendency to form complexes.

The *p*-block contains elements which are typical anionformers. It is the *p*-block that has all atoms which are in

organic ligands and which form the immediate environment of the central ion. Only eight elements of the *p*-block (Al, Ga, In, Tl, Ge, Sn, Pb and Bi) form cations.

Reagents

Sulphates of magnesium, aluminium, zirconium and thorium, 0.1 per cent solutions in 0.5 *M* sulphuric acid solution.
Arsenazo III, 0.05 per cent solution.
Sulphuric acid, 9 *M* solution.
Sodium acetate, 10 per cent solution.

Procedure. Take four cylinders and in each put 20 ml of metal sulphate solutions and 150 ml of water. Pour 10 ml of sodium acetate solution to a cylinder with magnesium sulphate solution and likewise to a cylinder with aluminium sulphate solution; pour 50 ml of sulphuric acid solution to a cylinder with zirconium sulphate solution and likewise to a cylinder with thorium sulphate solution. At the lecture, add 30 ml of arsenazo III solution to each cylinder and stir. A green colour appears in the cylinder with zirconium sulphate solution and likewise in the cylinder with thorium sulphate solution. Complexes are not formed in the cylinder with magnesium sulphate solution and likewise in the cylinder with aluminium sulphate solution, and the reagent retains its pink colour. Draw the attention of the audience to the fact that complexes of magnesium and aluminium with arsenazo III are not formed even in a weakly acid medium.

Note. Other organic reagents, such as PAN, sodium dithiocarbaminates and 8-hydroxyquinoline, may also be used to compare the action of a reagent on different ions in conformity with the position of the corresponding element in the periodic system.

Experiment 185. Interaction of Molybdenum (V) and Niobium (V) with the Thiocyanate Ion

Molybdenum is in the sixth group of the periodic system and, in compounds, manifests different oxidation states (0, 2+, 3+, 4+, 5+ and 6+). Depending on its oxidation state, the similarity between many of its compounds and

the compounds of other elements is observed. When its oxidation state is five, molybdenum manifests an analogy in respect to properties with niobium (V), which is in the fifth group (the properties of the element are displaced from right to left in the horizontal series of the periodic system). For example, molybdenum (V) and niobium (V) form coloured thiocyanate complexes, which are used for determining these elements.

Reagents

Sodium molybdate, solution containing 1 mg of MoO_3 in 1 ml.

Niobium pentoxide, solution containing 1 mg of Nb_2O_5 in 1 ml. 0.13 g of Nb_2O_5 is fused together with 2 g of potassium pyrosulphate; the melt is dissolved in 100 ml of 0.1 *M* tartaric acid solution, which is heated to boiling.

Tin dichloride, 25 per cent solution in 2 *M* hydrochloric acid solution.

Ammonium thiocyanate, 20 per cent solution.

Sulphuric acid, 5 *M* solution.

Procedure. In a cylinder, put 20 ml of sodium molybdate solution, 150 ml of water and 50 ml of sulphuric acid solution. In another cylinder, put 20 ml of niobium pentoxide solution, 150 ml of water and 50 ml of sulphuric acid solution. At the lecture, add 30 ml of tin chloride solution and 50 ml of ammonium thiocyanate solution to each cylinder. An intense red colour appears in the cylinder with molybdenum salt. A yellow-orange colour appears in the cylinder with niobium pentoxide solution.

Note. A similar regularity may be shown by taking the example of the ions of thorium (IV) and of uranium (IV), which form insoluble fluorides and complex compounds with organic reagents (arsenazo III). The displacement of the properties of the elements from left to right in the horizontal series may be shown by taking the example of the ions of cerium (IV) and hafnium (IV), which form precipitates with the ions IO_4^- and IO_3^-:

$$\begin{array}{cccc} Th(IV) & U(VI) & Ce(III) & Hf(IV) \\ \longleftarrow & U(IV) & Ce(IV) & \longrightarrow \end{array}$$

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